ISOMORPHISM WITHIN THE HEXAGONAL COLUMNAR MESOPHASE OF MOLECULAR AND MACROMOLECULAR SELF- AND CO-ASSEMBLED COLUMNS CONTAINING TAPERED GROUPS

by

D. Tomazos, R. Out, J. Heck, G. Johansson, V. Percec and M. Moeller

Published

in the

Department of Macromolecular Science
Case Western Reserve University
Cleveland, OH 44106-7202

DTIC QUALITY INSPECTED 2

June 30, 1994

94-20931

94 7 8 041

REPORT DOCUMENTATION PAGE

Public reporting burden for this collection of information is estimated to average 1 hour per response including the time for reviewing instructions searching existing data sources gathering and maintaining the data needed and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information including suggestions for reducing this burden to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503

1 AGENCY USE ONLY (Leave blank)	2. REPORT DATE June 30, 1994	3. REPORT TYPE AND DATES COVERED Abstract Report #3

4. TITLE AND SUBTITLE
Isomorphism Within the Hexagonal Columnar Mesophase of Molecular and Macromolecular Self- and Co-Assembled Columns Containing Tapered Groups

5. FUNDING NUMBERS
N00014-89-J-1828

6. AUTHOR(S)
D. Tomazos, R. Out, J. Heck, G. Johansson, V. Percec, and M. Moeller

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
Department of Macromolecular Science
Case Western Reserve University
Cleveland, OH 44106-7202

8. PERFORMING ORGANIZATION REPORT NUMBER
N00014-89-J-1828

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
Department of Navy
Office of Naval Research
800 North Quincy Street
Arlington, VA 22217-5000

10. SPONSORING/MONITORING AGENCY REPORT NUMBER
Abstract Report #3

11. SUPPLEMENTARY NOTES
Liquid Crystals, 16, 509 (1994)

12a. DISTRIBUTION/AVAILABILITY STATEMENT

12b. DISTRIBUTION CODE

13. ABSTRACT (Maximum 200 words)

The phase behaviour of binary mixtures of self assembled tapering molecules based on monoesters of oligooxyethylene glycol and 3,4,5-tris[4-n-dodecan-1-yloxy)benzyloxy]benzoic acid, their corresponding polymethacrylates, and of 4'-methyl (benzo-15-crown)-3,4,5-tris[4-n-dodecan-1-yloxy)benzyloxy]benzoate within their hexagonal columnar mesophase (Φ_h) is described. The binary blends between molecular tapers co-assemble into a single supramolecular column resulting in isomorphism within their Φ_h mesophase over the entire range of composition. The binary blends between polymethacrylates containing tapered side groups co-assemble into a single Φ_h phase only when the columns of the parent polymers are of similar diameters. This results in binary mixtures which are isomorphic within the Φ_h mesophase over the entire composition range. When the diameters of the columns formed by the parent polymers are dissimilar, isomorphic mixtures are obtained only over a narrow range of composition. Binary mixtures between molecular tapers and macromolecular systems containing tapered side groups co-assemble into a single column to the extent that intercalation of the molecular taper, within the column formed by the macromolecular system containing tapered side groups, is permissible. In all systems increased intra-columnar interactions can be induced by complexation of CF_3SO_3Li by the oligooxyethylenic receptors and specific crown ether receptors and CF_3SO_3Na as the third component are non-isomorphic within their Φ_h phase due to preferential complexation of the alkali metal cation by the column of the crown ether containing the molecular taper. This results in two columns of dissimilar diameters, which are isomorphic in the Φ_h phase only within a limited range of composition.

14. SUBJECT TERMS

15. NUMBER OF PAGES

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
unclassified	unclassified	unclassified	UL

Isomorphism Within the Hexagonal Columnar Mesophase of Molecular and Macromolecular Self- and Co-Assembled Columns Containing Tapered Groups

Dimitris Tomazos, Ron Out, James Heck, Gary Johansson, and Virgil Percec*

Department of Macromolecular Science

Case Western Reserve University

Cleveland, OH 44106-2699, USA

and

Martin Möller

Abteilung Organische Chemie III

Makromolekulare Chemie

Universität Ulm

Albert-Einstein-Alle 11

Postfach 4066, D-7900 Ulm, Germany

ABSTRACT

The phase behavior of binary mixtures of self-assembled molecular tapers based on monoesters of oligooxyethylene glycol and 3,4,5-tris[4-(n-dodecan-1-yloxy)benzyloxy]benzoic acid, their corresponding polymethacrylates, and of 4'-methyl (benzo-15-crown-5)-3,4,5-tris[4-(n-dodecan-1-yloxy)benzyloxy]benzoate within their hexagonal columnar mesophase (Φ_h) is described. The binary blends between molecular tapers co-assemble into a single supramolecular column resulting in isomorphism within their Φ_h mesophase over the entire range of composition. The binary blends between polymethacrylates containing tapered side groups co-assemble into a single Φ_h phase only when the columns of the parent polymers are of similar diameters. This results in binary mixtures which are isomorphic within the Φ_h mesophase over the entire composition range. When the diameters of the columns formed by the parent polymers are dissimilar, isomorphic mixtures are obtained only over a narrow range of composition. Binary mixtures between molecular tapers and macromolecular systems containing tapered side groups co-assemble into a single column to the extent that intercalation of the molecular taper, within the column formed by the macromolecular system containing tapered side groups, is permissible. In all systems increased intracolumnar interactions can be induced by complexation of $LiCF_3SO_3$ by the oligooxyethylenic receptors leading to isomorphism in otherwise non-isomorphic mixtures. Ternary mixtures between molecular tapers with non-specific oligooxyethylenic receptors and specific crown ether receptors and $NaCF_3SO_3$ as the third component are non-isomorphic within their Φ_h phase due to preferential complexation of the alkali metal cation by the column of the crown ether containing the molecular taper. This results in two columns of dissimilar diameters, which are isomorphic in the Φ_h phase only within a limited range of composition.

INTRODUCTION

Disc-like liquid crystals exhibiting thermotropic columnar mesophases have attracted recently considerable research interest.[1] Several reviews on this field of research have been published.[2-4] It is already accepted, contrary to what has been originally considered, that the presence of a flat rigid polyaromatic core, like for example in hexasubstituted triphenylenes,[3] is not a necessary requirement for the generation of molecules which exhibit columnar mesophases. Even compounds that can adopt a quasi-flat conformation by virtue of their conformational flexibility display columnar mesophases. Several examples of such compounds like octasubstituted cyclotetraveratrylene,[5] tetra- and hexasubstituted cyclic polyamines,[6] hexasubstituted scyllo-inositol (benzene-1,2,3,4,5,6-hexol),[7] hexakis(4-alkylphenoxymethyl)benzenes and hexakis(4-alkoxyphenyl)benzenes,[8] have been reported. In addition, even hexasubstituted cyclotriveratrylene derivatives,[9a-d] and tungsten-oxo calix[4]arene complexes,[9e] which have a cone-like and respectively a bowl-like shape, as well as compounds that structurally deviate from a strictly disc-like shape like biforked[10] and phasmidic[11] derivatives have been shown to form thermotropic columnar mesophases. Diablo compounds, i.e., molecules composed of two disc-like moieties interconnected by a rigid rod through their centers also exhibit columnar mesophases.[12]

Lyotropic columnar mesophases are also exhibited by many biological systems. An example is DNA which forms a lyotropic columnar hexagonal mesophase in water.[13] Supramolecular disc-like molecules exhibiting columnar mesophases were generated via molecular-recognition directed self-assembly of complimentary components.[14,15] Endo-recognition[14a] processes generated via both hydrogen bonding[14] and metal complexation[15] were used to produce disc-like molecules.

In biological systems, molecular recognition and self-assembly are the two main processes utilized by nature for the generation of supramolecular architectures with

remarkable properties. The utilization of these processes is exemplified by Tobacco Mosaic Virus (TMV) which is one of the best understood self-assembled biological systems.[14b,c,16] TMV consists of a single type of protein molecule (subunit) and a strand of RNA. The protein subunits can form single- or double-layered discs. In the presence of the RNA strand or below a specific pH value (in the absence of RNA) the self-assembled single- or double-layered discs assume a lock-washer shape which is required for the generation of the helical shaped single rod of TMV. The initial driving force for the self-assembly of TMV is therefore provided by exo-recognition by the tapered shape of the protein subunits followed by complimentary endo-recognition provided by the RNA strand.

The simplicity of this fascinating biological architecture has directed our research towards the development of synthetic approaches to the self-assembly of cylindrical supramolecular architectures by utilizing synthetic analogs which resemble those used by TMV. In the first series of experiments on this topic, we used a combination of exo-recognition generated by the taper shaped 3,4,5-tris[4-(n-dodecan-1-yloxy)benzyloxy]benzoate group and endo-recognition generated by a benzo-15-crown-5 endo receptor as a driving force for self-assembly.[17] The complexation of the benzo-15-crown-5 endo-receptor of 4'-methyl(benzo-15-crown-5)-3,4,5-tris[4-(n-dodecan-1-yloxy)benzyloxy]benzoate with $NaCF_3SO_3$ or KCF_3SO_3 destabilizes its crystalline phase and induces its self-assembly into a cylindrical architecture which displays an enantiotropic thermotropic columnar hexagonal (Φ_h) mesophase.[17] In a simpler and more general approach, we have utilized compounds which are derived from 4'-methyl(benzo-15-crown-5)-3,4,5-tris[4-(n-dodecan-1-yloxy)benzyloxy]benzoate by replacing its selective benzo-15-crown-5 endo receptor with the non-selective hydroxyoligooxyethylene group containing from one to four oxyethylene repeat units.[18a] The hydroxyl terminated oligooxyethylenic endo-receptor functions by a combination of hydrogen bonding and

3

alkali metal salt complexation, while exo-recognition is provided by the tapered shape to induce the self-assembly into a cylindrical supramolecular architecture which displays a hexagonal columnar (Φ_h) mesophase. The nonselective complexation of metal salts enhances the endo-recognition and therefore the driving force for self-assembly as being reflected in the increased Φ_h-isotropic (Φ_h-I) transition temperatures of the complexes versus those of the parent uncomplexed compounds. The corresponding polymethacrylates of the hydroxyl terminated compounds allowed, for the first time, a comparison between a "molecular" and a "supramolecular" polymer backbone effect to be made.[18a] Both in polymethacrylates containing tapered side groups,[18a] as well as in other similar polymer systems[18b,c] the endo recognition process ("supramolecular" backbone) was replaced by a polymer ("molecular") backbone.

Presently, we are investigating the phase behavior of binary mixtures of various molecular, macromolecular, and supramolecular systems which self-assemble into cylinders displaying a Φ_h mesophase. A general discussion on isomorphism in crystalline and liquid crystalline phases of polymers and copolymers is available elsewhere.[19] The goal of this paper is to discuss the isomorphism of binary mixtures of monoesters of oligooxyethylene glycol with 3,4,5-tris[4-(n-dodecan-1-yloxy)benzyloxy]benzoic acid, of their corresponding polymethacrylates, and of 4'-methyl(benzo-15-crown-5)-3,4,5-tris[4-(n-dodecan-1-yloxy)benzyloxy]benzoate within their Φ_h mesophase using results obtained by a combination of differential scanning calorimetry (DSC) and thermal optical polarized microscopy. The phase behavior of ternary mixtures with $LiCF_3SO_3$ or $NaCF_3SO_3$ as the third component will also be discussed.

EXPERIMENTAL

Materials

$LiCF_3SO_3$ (97%, Aldrich) was dried under vacuum at 120°C for 24 hrs and stored

in a desiccator. $NaCF_3SO_3$ was prepared as described previously.[17] CH_2Cl_2 was distilled from CaH_2. Tetrahydrofuran (THF) was distilled from $LiAlH_4$ under dry nitrogen.

Synthesis of Molecular and Macromolecular Compounds Containing Tapered Groups

Details of the syntheses of the monoesters of oligooxyethylene glycol with 3,4,5-tris[4-(n-dodecan-1-yloxy)benzyloxy]benzoic acid, of their corresponding polymethacrylates,[18a] and of 4'-methyl(benzo-15-crown-5)-3,4,5-tris[4-(n-dodecan-1-yloxy)benzyloxy]benzoate[17] were reported previously.

Preparation of Binary Mixtures

Binary mixtures were prepared by weighing the individual components in cleaned and dried glass vials and then adding dry CH_2Cl_2 to an equal final volume so as to obtain a homogeneous solution. The solvent was removed under a gentle stream of dry nitrogen, and the vials were placed in a vacuum desiccator at 0.5 mmHg for 12 hrs.

Ternary mixtures with $LiCF_3SO_3$ or $NaCF_3SO_3$ as the third component were prepared in a similar manner, with the exception that CH_2Cl_2 was replaced by dry THF in order to form a homogeneous solution. In this case, after evaporation of the solvent, the vials were evacuated at 0.5 mm Hg for at least 24 hrs.

Techniques

A Perkin Elmer DSC-4 differential scanning calorimeter equipped with a TADS data station was used to determine the thermal transitions which were reported as the maximum and minimum of their endothermic and exothermic peaks. In all cases, heating and cooling rates were 20°C/min. Second and subsequent heating scans and first and subsequent cooling scans were identical. A Carl-Zeiss optical polarized microscope (magnification

100x) equipped with a Mettler FP82 hot stage and a Mettler FP80 central processor was used to observe the thermal transitions and to analyze the anisotropic textures.

RESULTS AND DISCUSSION

To date only very few investigations on the isomorphism of discotic liquid crystals within their columnar mesophase have been reported. One example refers to the isomorphism of binary mixtures of symmetric hexakis(n-pentyloxy)triphenylene with asymmetric 3,4,3',4'-tetrakis(n-pentyloxy)-3",4"-bis(n-nonyloxy)triphenylene.[20] The binary mixtures of these compounds are isomorphic in their columnar mesophase over the entire range of compositions. Interestingly, the columnar hexagonal-isotropic transition (Φ_h-I) composition dependence of the phase diagram of these mixtures displays an azeotropic minimum. A second example of isomorphism was discussed for mixtures of disc-like molecules based on the flexible core of cyclotetraveratrylene.[21] The mixtures resulting from cocyclotetramerization of 3,4-bis(n-hexyloxy)benzyl alcohol and bis(n-dodecanyloxy)benzyl alcohol are statistical mixtures of six possible isomers of octasubstituted cyclotetraveratrylene. Regardless of composition, all mixtures were found to be isomorphic within their columnar mesophase. Both examples deal with molecular disc-like liquid crystals.

In the present investigation, the formation of the hexagonal columnar mesophase is the result of self-assembly of molecular taper shaped groups and of macromolecules containing tapered side groups via molecular recognition processes.

The chemical structures of all compounds which will be used in the present study are summarized in Scheme 1. All low molar mass compounds based on hydroxyl terminated oligooxyethylene segments and 3,4,5-tris[4-(n-dodecan-1-yloxy)benzyloxy]benzoate moieties (1-4) self-assemble into supramolecular cylinders

6

which display enantiotropic hexagonal columnar (Φ_h) mesophases. Their self-assembly is a result of two processes. Exo-recognition, which is provided by their tapered shape and endo-recognition, which results via H-bonding of their -OH terminated oligooxyethylenic segments (Scheme 1).[18a] Their polymeric analogues (**P1-P4**) also self-assemble into cylindrical architectures which exhibit an enantiotropic Φ_h mesophase. In these compounds, the endo-recognition previously provided by H-bonding is replaced by the covalent attachment of the tapers onto a polymethacrylate backbone.[18a] Since this is a covalent interaction, **P1-P4** have higher Φ_h-I transition temperatures ($T_{\Phi h\text{-}I}$) than that of **1-4**, respectively. The average column diameters of self-assembled cylinders from **1-4** and **P1-P4** were determined by X-ray scattering experiments and their thermal transitions were determined by DSC (Table 1). The compound 4'-methyl(benzo-15-crown-5)-3,4,5-tris[4-(n-dodecan-1-yloxy)benzyloxy] benzoate (**5**) is only crystalline (Table 1). The crown ether moiety can complex alkali metal ions, and thus, functions as an endo-receptor. This interaction leads to the suppression of its crystalline phase and to the generation of an enantiotropic columnar mesophase.[17] Its thermal transitions are also summarized in Table 1.

Binary mixtures between molecular tapers of monoesters of oligoethylene glycol with 3,4,5-tris[4-(n-dodecan-1-yloxy)benzyloxy]benzoic acid

Figure 1 presents the phase behavior of the binary mixture of **1** and **4**. During both heating and cooling (Figure 1a) DSC scans, $T_{\Phi h\text{-}I}$ of this binary mixture exhibits an almost linear dependence on composition. The experimental data of $T_{\Phi h\text{-}I}$ from the phase diagram in Figure 1a can be compared with the data calculated using the Schroeder-van Laar equation[22] which applies to first-order transitions of ideal binary mixtures:

$$F_1 = \left\{ 1 - \frac{\Delta H_1^0 T_2 (T\text{-}T_1)}{\Delta H_2^0 T_1 (T\text{-}T_2)} \right\}^{-1}$$

where F_1 is the molar fraction of component 1, T_1 and ΔH_1 are the transition temperature and the enthalpy change of pure component 1, T_2 and ΔH_2 have the same meaning for component 2, while T is the transition temperature corresponding to composition F_1. An excellent agreement between experimental and calculated $T_{\Phi_h\text{-}I}$ values is observed. The enthalpy changes (ΔH) associated with $T_{I\text{-}\Phi_h}$ and $T_{\Phi_h\text{-}K}$ from the cooling scans are presented in Figure 1b and, within experimental error, they seem to be independent of composition.

The binary mixtures of **2** and **4** (Figure 2a,b) and of **3** and **4** (Figure 3a,b) display a similar behavior to the binary mixture of **1** with **4**. In all binary mixtures, the experimentally determined $T_{\Phi_h\text{-}I}$ data are in agreement with the respective data calculated using the Schroeder-van Laar equation. This result demonstrates that all binary mixtures of compounds **1-4** are isomorphic within their Φ_h mesophase. The isomorphism of these compounds within their Φ_h phase is not unexpected since all of them possess the required features for self-assembly into a single column, i.e., exo-recognition provided by the tapered shape and endo-recognition provided by hydrogen bonding.[18a] Both interactions facilitate the intercalation of various mixtures of compounds **1** to **4** into a column of intermediary diameter between those of the parent compounds. A schematic representation of the co-assembly of compounds **1** and **4** within the same supramolecular column is shown in Scheme 2. Since the only difference between these compounds is the length of their flexible oligooxyethylene segment, it is expected that it should have very little or no effect at all on their ability to mix in a single column.

Binary mixtures between polymethacrylates containing tapers of monoesters of oligoethylene glycol with 3,4,5-tris[4-(n-dodecan-1-yloxy)benzyloxy]benzoic acid

The thermal transitions of the binary mixture of polymers **P1** and **P4** that assemble into columns of dissimilar diameters (Table 1) are presented in Figure 4a (data from second heating scan) and 4b (data from first cooling scan). At low mole% compositions in **P1**, the two polymers form mixtures that exhibit a single Φ_h-I transition. Above a composition of about 40 mole% of **P1**, the binary mixture displays two Φ_h-I transitions which are almost identical to the respective transitions of each individual polymer. This behavior suggests that above this composition, the two polymers are non-isomorphic within their Φ_h mesophase. While this behavior is not trivial, a possible explanation can be drawn if one considers the formation of the Φ_h mesophase by these polymers. Although additional experimental support is required, we can assume that the formation of each individual column arises from the self-assembly of a single polymer chain since the possibility of having two polymer chains occupying the inner core of the same column should be both energetically and kinetically unfavorable. Therefore, based on this assumption, columns should be formed from each individual polymer. Consequently, any mixture between polymers **P1** and **P4** should be composed of columns of two dissimilar diameters (Table 1). Scheme 3 represents two extreme situations of binary mixtures between **P1** and **P4**. In Scheme 3a, a small number of larger diameter columns (**P4**) is introduced into the hexagonal arrangement of smaller diameter columns (**P1**). This composition is expected to distort the hexagonal packing as shown by the irregular hexagon drawn in Scheme 3. In Scheme 3b, a small number of smaller diameter columns (**P1**) is introduced into the hexagonal arrangement of larger diameter columns (**P4**). As is schematically shown, this composition does not distort much the packing into a hexagonal arrangement. Figure 4c presents the enthalpy changes associated with the $T_{I-\Phi_h}$, $T_{\Phi_h-\Phi_h}$ and T_{Φ_h-K} transitions from the cooling scan of this binary polymer mixture between **P1** and **P4** as a function of composition.

The thermal transitions of the binary mixture of **P3** and **P4** as a function of mole%

9

composition are plotted in Figure 5a (data from the second heating scan) and Figure 5b (data from the cooling scan). For all compositions, the two polymers exhibit a single Φ_h-I transition on their cooling scans (Figure 5b). The heating scans of the binary mixtures present a single broad Φ_h-I transition the maximum of which is plotted as a function of mole% composition in P3 in Figure 5a. The single Φ_h-I transition on both heating and cooling scans suggests that the two polymers P3 and P4 which form columns with very similar diameters (Table 1) are isomorphic within the whole range of composition of their binary mixtures. This is expected since the introduction of columns with similar diameter into a hexagonal arrangement should not distort their packing. Figure 5c presents the ΔH of all transitions as a function of composition for the binary mixture P3/P4 as determined from first cooling scans.

Binary mixtures between molecular tapers and polymethacrylates containing tapers of monoesters of oligoethylene glycol with 3,4,5-tris[4-(n-dodecan-1-yloxy)benzyloxy]benzoic acid as side groups

The binary mixture of polymer P3 containing a triethyleneoxide spacer and the hydroxyl terminated low molecular weight compound 3 with the same length of the oligooxyethylenic segment exhibits the phase behavior presented in Figure 6. Up to a composition of about 40 mole% of 3, a single Φ_h-I transition is observed in both heating (Figure 6a) and cooling (Figure 6b) scans. This behavior suggests that the low molecular weight compound 3 becomes intercalated within the column formed by polymer P3. Above a composition of about 40 mole%, the excess 3 that cannot be intercalated within the polymer structure self-assembles giving rise to a second Φ_h-I transition at a lower temperature (Figure 6a,b). The previous statement is supported by the fact that this Φ_h-I transition remains constant with increasing concentration of 3. At the same time, the highest temperature Φ_h-I transition appears to be constant also above 40 mole% of 3,

10

suggesting that this value represents the maximum amount of **3** that has been intercalated within the column generated by **P3**. Scheme 4 illustrates the co-assembly of **3** into the column of **P3** via endo-recognition. The enthalpy changes of the Φ_h-K and I-Φ_h transitions determined from the cooling scan are plotted in Figure 6c. The binary mixture between **P2** and **3** behaves in a similar manner as indicated by the data plotted in Figure 7a,b.

Ternary mixtures between molecular tapers and polymethacrylates containing tapers of monoesters of oligoethylene glycol with 3,4,5-tris[4-(n-dodecan-1-yloxy)benzyloxy]benzoic acid containing $LiCF_3SO_3$ as the third component

The effect of complexation of $LiCF_3SO_3$ on the phase transitions of a binary mixture containing 10 mole% of **P3** and 90 mole% of **3** is illustrated in Figure 8. The uncomplexed mixture of **P3** and **3** exhibits two Φ_h-I transitions arising from the columns self-assembled from each individual component (Figure 8). The data from the first heating scan are presented in Figure 8a and resemble the phase behavior of the pure **3** complexed with $LiCF_3SO_3$.[18a] This is not unexpected since the binary mixture contains 90 mole% of compound **3**. It also indicates that the ability of **3** to complex $LiCF_3SO_3$ is much higher than that of **P3**. The complexation ability of the oligooxyethylenic group of **3** is higher than that of the corresponding unit of **P3** most probably due to its higher Lewis base character. Second and subsequent heating (Figure 8b) and first and subsequent cooling (Figure 8c) scans are different. At low $LiCF_3SO_3$ concentrations, two Φ_h-I transitions are observed. The lowest temperature Φ_h mesophase, attributed to **3**, is affected the most since its transition temperature clearly increases with increasing the amount of $LiCF_3SO_3$ (Figures 8b,c). At a concentration of 0.1 mole $LiCF_3SO_3$/mole of ethyleneoxide repeat unit and above, the two Φ_h-I transitions merge into a single one. This transition increases

slightly with the increase of $LiCF_3SO_3$ content in the mixture and then becomes essentially independent of the amount of $LiCF_3SO_3$. This behavior demonstrates that the introduction of salt enhances the co-assembly between **P3** and **3** due to complexation. The co-assembly of the tapered **3** into the self-assembled column of **P3** transforms the immiscible mixture of **3** and **P3** into a miscible one. The enthalpy changes (ΔH) of all transitions from the cooling scan of this mixture are plotted in Figure 8d.

Binary mixtures between molecular tapers based on 3,4,5-tris[4-(n-dodecan-1-yloxy)benzyloxy]benzoic acid with oligoethylene glycol and 15-crown-5 endo-receptors, and their ternary mixture with $NaCF_3SO_3$ as the third component

The behavior of binary mixtures of compounds **2** and **5** was also examined. Compounds **2** and **5** have the same tapered unit but two different endo receptors (Scheme 1). Compound **2** has a hydroxyl terminated diethyleneoxide repeat unit as endo receptor, while compound **5** has a benzo-15-crown-5 receptor. Compound **2** displays an enantiotropic Φ_h mesophase.[18a] In contrast, compound **5** displays a layered crystalline phase.[17] The binary mixtures of **2** and **5** exhibit a monotropic Φ_h mesophase up to a composition of 40 mole% of **5** (Figures 9a,b). A linear dependence of the $I-\Phi_h$ transition as a function of composition is observed (Figure 9b). This suggests that **2** and **5** are miscible within their Φ_h mesophase. A linear dependence is also observed for the corresponding $\Delta H_{I-\Phi_h}$ (Figure 9c). In their DSC scans, these mixtures exhibit a monotropic Φ_h phase and multiple melting transitions which most probably arise from an eutectic mixture (Figure 9a). A similar behavior is observed in the binary mixture of **4** (with a hydroxyl terminated tetraethyleneoxide repeat unit segment) and **5** (Figure 10a,b,c).

Previous experiments involving the complexation of compound **5** with $NaCF_3SO_3$ and KCF_3SO_3 have shown that the crystalline phase of this compound is destabilized upon

complexation.[17] In addition, complexation induces its self-assembly into a columnar architecture which displays an enantiotropic Φ_h mesophase.[17] It was therefore interesting to examine how an equimolar mixture of 5 with 2 behaves upon complexation with $NaCF_3SO_3$. Figure 11a and b plots the phase transition temperatures as a function of the molar content of $NaCF_3SO_3$ per mole of 5 obtained from second heating and first cooling DSC scans, respectively. The equimolar mixture of 2 and 5 without $NaCF_3SO_3$ is only crystalline. Upon complexation with $NaCF_3SO_3$, a monotropic Φ_h mesophase is obtained up to 0.2 mole of $NaCF_3SO_3$/mole of 5 (Figure 11b). Above this value, all mixtures display two distinct Φ_h mesophases during both heating and cooling scans (Figure 11a,b). Although this behavior is not trivial, it can be explained if one considers the complexation ability of a crown ether in comparison to that of an oligooxyethylene glycol.[23] Since the crown ether is more selective and binds ions much stronger than the glycol, the phase behavior of the mixture can be explained by considering the presence of two distinct components. One is the complexed compound 5, the other is the mixture of remaining uncomplexed 2 and 5. Therefore, the single Φ_h transition present up to a value of 0.2 mole of $NaCF_3SO_3$/mole of 5 arises entirely from the complexed 5. As the concentration of $NaCF_3SO_3$ increases, the relative mole% of 5 in the remaining uncomplexed mixture of 2 and 5 decreases, since free 5 is transformed into complexed 5. This gives rise to the second Φ_h mesophase of the mixture of free 5 and 2, which also increases with the amount of $NaCF_3SO_3$ since the mole% of free 5 decreases at a constant mole% of 2 (the phase behavior of the mixture of 2 with 5 presented in Figure 9). In addition, the complex between 5 and $NaCF_3SO_3$ is very strong and should result in a rigid column. This statement is supported by the fact that complexes of 5 with salt display a glass transition in their DSC scans.[17] The increased rigidity of the column of complexed 5 and the very weak competition of the oligooxyethylenic endo-receptor of compound 2 for Na^+, as compared to that of the crown ether receptor of 5, should prohibit the intercalation of 2 within the

column of complexed **5**. This results in the formation of two columns of dissimilar diameters (one consisting of the complex of **5** with Na⁺ and the other consisting of the mixture of **2** and uncomplexed **5**), and consequently, to the observed absence of isomorphism.

CONCLUSIONS

The present results highlight the effect of structural factors on the isomo... ism of self-assembled supramolecular liquid crystals within their hexagonal columnar (Φ_h) mesophases. Our investigation indicates that the primary factors in obtaining isomorphism in binary mixture is the diameter of the column formed by the self-assembly of the individual compounds as well as the ability of interaction within the inner core of the columns. Low molecular weight compounds with the same length alkyl tails and segments that can interact in the inner core of the column co-assemble into cylinders which are completely isomorphic within their Φ_h phase. In contrast, polymeric compounds are miscible only if their column diameters are approximately the same. When their column diameters are dissimilar, the two polymers are miscible only at low mole% contents of the *component forming the smaller diameter column*. Mixtures between low molar mass and polymeric components are miscible up to the extent that intercalation of the low molar compound into the polymeric structure is permitted. Mixtures that are immiscible can become miscible by increasing the strength of interaction within the inner core of the columnar architecture. In the present case, this was accomplished by alkali metal salt complexation. Finally, preferential interaction in the inner part of the column of the one component in mixtures of low molar mass compounds can induce immiscibility if the second component can interact only weakly with the first. This was shown by the selective complexation of alkali metal ions by a crown ether moiety versus the non-selective complexation by an oligooxyethylene glycol moiety. In an unrelated study involving main

14

chain and side chain discotic liquid crystalline polymers, the induction of hexagonal columnar mesomorphism, its enhancement, and the induction of compatibility and mesomorphism in an incompatible polymer mixture via electron-donor acceptor interactions were reported.[4,24] The enhancement of mesomorphism of liquid crystalline polymers via non-covalent interactions was recently reviewed.[25]

The present results provide insight in the manipulation of phase transitions in self-assembled liquid crystals displaying columnar hexagonal mesophases. This study is important since it provides complementary information for future research on these supramolecular architectures. As such, one can foresee interest in mesomorphic ionic electrolytes, semiconductor nanocluster arrays, reactions in spatially confined dipolar solvent media including polymerization in hexagonal columnar organized phases, etc.

ACKNOWLEDGMENTS

REFERENCES

1. (a) S. Chandrasekhar, B. K. Sadashiva and K. A. Suresh, *Pramana,* 1977, **9**, 471; (b) J. Billard, J. C. Dubois, N. H. Tinh and A. Zann, *Nouv. J. Chim.,* 1978, **2**, 535; (c) N. H. Tihn, J. C. Dubois, J. Malthete, C. Destrade, *C. R . Acad. Sci. Paris,* 1978, **286C**, 463; (d) C. Destrade, M. C. Mondon and J. Malthete. *J. Phys. C (Paris),* 1979, **3**, 17.

2. (a) S. Chandrasekhar, in *Advances in Liquid Crystals,* ed. G. H. Brown, Academic Press, New York London, 1982, vol. 5, p. 47; (b) S. Chandrasekhar, *Philos. Trans. R. Soc. London, Ser. A ,* 1983, **309**, 93; (c) S. Chandrasekhar and G. S. Ranganath, *Rep. Prog. Phys.,* 1990, **53**, 57; (d) S. Chandrasekhar, *Liq.*

Cryst., 1993, **14**, 3.

3. (a) J. C. Dubois and J. Billard, in *Liquid Crystals and Ordered Fluids*, ed. A. C. Griffin and J. F. Johnson, Plenum Press, New York, 1984, 4, p. 1043; (b) A. Demus, *Liq. Cryst.*, 1989, **5**, 75.

4. H. Ringsdorf and R. Wustefeld, *Philos. Trans. R. Soc. London, Ser. A* , 1990, **330**, 95.

5. (a) H. Zimmermann, R. Poupko, Z. Luz and J. Billard, *Liq. Cryst.*, 1988, **3**, 759; (b) V. Percec, C. G. Cho and C. Pugh, *J. Mater. Chem.*, 1991, **1**, 217; (c) V. Percec, C. G. Cho, C. Pugh and D. Tomazos, *Macromolecules*, 1992, **25**, 1164.

6. (a) J. M. Lehn, J. Malthete and A. M. Levelut, *J. Chem. Soc, Chem. Commun.*, 1985, 1794; (b) C. Mertesdorf and H. Ringsdorf, *Liq. Cryst.*, 1989, **5**, 1757; (c) C. Mertesdorf, H. Ringsdorf and J. Stumpe, *Liq. Cryst.*, 1991, **9**, 337; (d) G. Lattermann, *Liq. Cryst.*, 1989, **6**, 619; (e) G. Lattermann, *Mol. Cryst. Liq. Cryst.*, 1990, **182b**, 299; (f) D. Tatarsky, K. Banerjee and W. T. Ford, *Chem. Mater.*, 1990, **2**, 138; (g) S. H. J. Idziak, N. C. Maliszewskyj, P. A. Heiney, J. P. McCauley Jr., P. A. Sprengeler and A. B. Smith III, *J. Am. Chem. Soc.*, 1991, **113**, 7666; (h) A. Liebmann, C. Mertesdorf, T. Plesnivy, H. Ringsdorf and H. Wendorff, *Angew. Chem.. Int. Ed. Engl.*, 1991, **30**, 1375; (i) S. H. J. Idziak, N. C. Maliszewskyj, G. B. M. Vaughan, P. A. Heiney, C. Mertesdorf, H. Ringsdorf, J. P. McCauley Jr. and A. B. Smith III, *J. Chem. Soc. Chem. Commun.*, 1992, 98.

7. (a) B. Kohne, K. Praefcke and J. Billard, *Z. Naturforsch. Teil B*, 1986, **41**, 1036; (b) B. Kohne, K. Praefcke, P. Psaras and W. Stephan, *Chimia*, 1987, **41**, 63; (c) H. W. Newling, H. Stegemeyer, K. Praefcke and B. Kohne, *Z. Naturforsch. Teil A*, 1987. **42A**, 631.

8. C. Pugh and V. Percec, *J. Mater. Chem.*, 1991, **1**, 765.

9. (a) J. Malthete and A. Collet, *Nouv. J. Chim.*, 1985, **9**, 151; (b) A. M. Levelut, J. Malthete and A. Collet, *J. Phys.*, 1986, **47**, 351; (c) J. Malthete and A. Collet, *J. Am. Chem. Soc.*, 1987, **109**, 7544; (d) H. Zimmermann, R. Poupko, Z. Lutz and J. Billard, *Z. Naturforsch . Teil A*, 1985, **40**, 149; (e) B. Xu and T. M. Swager, *J. Am. Chem. Soc.*, 1993, **115**, 1159.

10. (a) H. T. Nguyen, C. Destrade, A. M. Levelut and J. Malthete, *J. Phys.*, 1986, **47**,553; (b) C. Alstermark, M. Eriksson, M. Nilsson, C. Destrade and H. T. Nguyen, *Liq. Cryst.*, 1990, **8**, 75; (c) C. Destrade, H. T. Nguyen, C. Alstermark, G. Lindsten, M. Nilsson and B. Ottenholm, *Mol. Cryst. Liq. Cryst.*, 1990, **180B**, 265.

11. (a) J. Malthete, A. M. Levelut and N. H. Tinh, *J. Phys. Lett.*, 1985, **46**, L875; (b) J. Malthete, N. H. Tinh and A. M. Levelut, *J. Chem. Soc. Chem. Commun.*, 1986, 1548; (c) D. Guillon, A. Skoulios and J. Malthete, *Europhys. Lett.*, 1987, **3**, 68; (d) J. Malthete, A. Collet and A. M. Levelut, *Liq. Cryst.*, 1989, **5**, 123.

12. J. Malthete and A. M. Levelut, *Adv. Mater.*, 1991, **3**, 94.

13. F. Livolant, A. M. Levelut, J. Doucet and J. P. Benoit, *Nature*, 1989, **339**, 724.

14. (a) J. M. Lehn, *Angew. Chem. Int. Ed. Engl.*, 1990, **29**, 1304;(b) J. S. Lindsey, *New J. Chem.*, 1991, **15**, 153; (c) G. M. Whitesides, J. P. Matias and C. T. Seto, *Science*, 1991, **254**, 1312; (d) M. J. Brienne, J. Gebard, J. M. Lehn and J. Stibor, *J. Chem. Soc. Chem. Commun.*, 1989, 1868; (e) C. Fouquey, J. M. Lehn and A. M. Levelut, *Adv. Mater.*, 1990, **2**, 254; (f) G. Latterman and G. Staufer, *Liq. Cryst.*, 1989, **4**, 347; (g) G. Latterman, G. Staufer and G. Brezesinski, *Liq. Cryst.*, 1991, **10**, 169; (h) K. Praefcke, B. Kohne, B. Gundogan, D. Demus, S. Diele and G. Pelzl, *Mol. Cryst. Liq. Cryst. Lett.*, 1990, **7**, 27.

15. (a) A. M. Giroud-Godquin and P. M. Maitlis, *Angew. Chem. Int. Ed. Engl.*, 1991, **30**, 375; (b) J. Barbera, C. Cativiela, J. L. Serrano and M. M. Zurbano,

17

Adv. Mater., 1991, **3**, 602; (c) C. K. Lai, A. G. Serrette and T. M. Swager, *J. Am. Chem. Soc.*, 1992, **114**, 7948.

16. A. Klug, *Angew. Chem. Int. Ed. Engl.*, 1983, **22**, 565.

17. V. Percec, G. Johansson, J. Heck and G. Ungar, *J. Chem. Soc. Perkin Trans.1*, in press.

18. (a) V. Percec, J. Heck, D. Tomazos, F. Falkenberg, H. Blackwell and G. Ungar, *J. Chem. Soc. Perkin Trans.1*, submitted; (b) V. Percec, M. Lee, J. Heck, H. Blackwell, G. Ungar and A. Alvarez-Castillo, *J. Mater. Chem.*, 1992, **2**, 931; (c) V. Percec, J. Heck, M. Lee, G. Ungar and A. Alvarez-Castillo, *J. Mater. Chem.*, 1992, **2**, 1033.

19. V. Percec and Y. Tsuda, *Polymer*, 1991, **32**, 661.

20. H. T. Nguyen, M. C. Bernaud, G. Sigaud and C. Destrade, *Mol. Cryst. Liq. Cryst.*, 1981, **65**, 307.

21. V. Percec, C. G. Cho, C. Pugh and D. Tomazos, *Macromolecules*, 1992, **25**, 1164.

22. T. Schroeder, *Z. Phys. Chem.*, 1893, **11**, 449; J. J. Van Laar, *Z. Phys. Chem.*,1908, **63**, 216; G. R. Van Hecke, *J. Phys. Chem.*, 1979, **83**, 2344; M. F. Achard, M. Mauzac, M. Richard, M. Sigaud and F. Hardouin, *Eur. Polym. J.*, 1989, **25**, 593.

23. G. W. Gokel, D. M. Goli and R. A. Schultz, *J. Org. Chem.*, 1983, **48**, 2837 and references cited therein.

24. H. Ringsdorf, R. Wustefeld, E. Zerta, M. Ebert and J. H. Wendorff, *Angew. Chem. Int. Ed. Engl.*, 1989, **28**, 914.

25. a) V. Percec, H. Jonsson and D. Tomazos, *"Reactions and Interactions in Liquid Crystalline Media"* in *"Polymerization in Organized Media"*, C. M. Paleos Ed., Gordon and Breach, New York, 1992, p. 1-104; b) V. Percec and D. Tomazos,

FIGURE AND SCHEME CAPTIONS

Scheme 1.   The structures of the monoesters of oligooxyethylene glycol with 3,4,5-tris[4-(n-dodecan-1-yloxy)benzyloxy]benzoic acid (**1-4**), of their corresponding polymethacrylates (**P1-P4**), and of 4'-methyl(benzo-15-crown-5)-3,4,5-tris[4-(n-dodecan-1-yloxy)benzyloxy]benzoate (**5**).

Scheme 2.   Schematic representation of the co-assembly of **1** and **4** into the same columnar arrangement.

Scheme 3.   a) Schematic representation of the columnar hexagonal arrangement resulting from the introduction of a small amount of larger diameter columns into an excess of smaller diameter columns (the resulting distortion is illustrated by the irregular hexagon).

b) Schematic representation of the columnar hexagonal arrangement resulting from the introduction of a small amount of smaller diameter columns into an excess of larger diameter columns (in this case, the arrangement does not become distorted).

In both (a) and (b) parts, the circle diameters have been drawn proportional to the ones calculated for **P1** and **P4** from X-ray scattering data.

Scheme 4.   Schematic representation of the co-assembly of **3** into the column formed by the self-assembly of **P3**.

Figure 1.   a) The dependence of phase transition temperatures on composition for the binary mixture of **1** with **4** as determined from second heating scan ($\square$, $T_{K-\Phi h}$), ($\bigcirc$, $T_{\Phi h-I}$); first cooling scan ($\bullet$, $T_{I-\Phi h}$), ($\blacksquare$, $T_{\Phi h-K}$); calculated by

19

the Schroeder-van Laar equation for the data corresponding to second heating scans (+).

b) The dependence of ΔH associated with the transition temperatures of the binary mixture of **1** with **4** from first cooling scan ($\bullet$, $\Delta H_{I\text{-}\Phi h}$), ($\blacksquare$, $\Delta H_{\Phi h\text{-}K}$).

Figure 2.   a) The dependence of phase transition temperatures on composition for the binary mixture of **2** with **4** as determined from second heating scan ($\square$, $T_{K\text{-}\Phi h}$), ($\bigcirc$, $T_{\Phi h\text{-}I}$); first cooling scan ($\bullet$, $T_{I\text{-}\Phi h}$), ($\blacksquare$, $T_{\Phi h\text{-}K}$); calculated by the Schroeder-van Laar equation for the data corresponding to second heating scans (+).

b) The dependence of ΔH associated with the transition temperatures of the binary mixture of **2** with **4** from first cooling scan ($\bullet$, $\Delta H_{I\text{-}\Phi h}$), ($\blacksquare$, $\Delta H_{\Phi h\text{-}K}$).

Figure 3.   a) The dependence of phase transition temperatures on composition for the binary mixture of **3** with **4** as determined from second heating scan ($\square$, $T_{K\text{-}\Phi h}$), ($\bigcirc$, $T_{\Phi h\text{-}I}$); first cooling scan ($\bullet$, $T_{I\text{-}\Phi h}$), ($\blacksquare$, $T_{\Phi h\text{-}K}$); calculated by the Schroeder-van Laar equation for the data corresponding to second heating scans (+).

b) The dependence of ΔH associated with the transition temperatures of the binary mixture of **3** with **4** from first cooling scan ($\bullet$, $\Delta H_{I\text{-}\Phi h}$), ($\blacksquare$, $\Delta H_{\Phi h\text{-}K}$).

Figure 4.   The dependence of phase transition temperatures on composition for the binary mixture of **P1** with **P4**. a) second heating scan ($\square$, $T_{K\text{-}\Phi h}$), ($\bigcirc$, $T_{\Phi h\text{-}\Phi h}$), ($\bigcirc$, $T_{\Phi h\text{-}I}$); b) first cooling scan ($\bullet$, $T_{I\text{-}\Phi h}$), ($\bullet$, $T_{\Phi h\text{-}\Phi h}$), ($\blacksquare$, $T_{\Phi h\text{-}K}$); c) the dependence of ΔH associated with the transition temperatures of the binary mixture of **P1** with **P4** from first cooling scan ($\bullet$, $\Delta H_{I\text{-}\Phi h}$),

(●, $\Delta H_{\Phi h-\Phi h}$), (■, $\Delta H_{\Phi h-K}$).

Figure 5. The dependence of phase transition temperatures on composition for the binary mixture of **P3** with **P4**. a) second heating scan (❑, $T_{K-\Phi h}$), (○, $T_{\Phi h-\Phi h}$), (○, $T_{\Phi h-I}$), (+, calculated by the Schroeder-van Laar equation); b) first cooling scan (●, $T_{I-\Phi h}$), (■, $T_{\Phi h-K}$), (+, calculated by the Schroeder-van Laar equation); c) the dependence of ΔH associated with the transition temperatures of the binary mixture of **P3** with **P4** from first cooling scan (●, $\Delta H_{I-\Phi h}$), (■, $\Delta H_{\Phi h-K}$).

Figure 6. The dependence of phase transition temperatures on composition for the binary mixture of **P3** with **3**. a) second heating scan (❑, T_{K-K}), (❑, $T_{K-\Phi h}$), (Δ, $T_{\Phi h-\Phi h}$), (○, $T_{\Phi h-I}$); b) first cooling scan (●, $T_{I-\Phi h}$), (▲, $T_{\Phi h-\Phi h}$), (■, $T_{\Phi h-K}$); c) the dependence of ΔH associated with the transition temperatures of the binary mixture of **P3** with **3** from first cooling scan (●, $\Delta H_{I-\Phi h}$), (▲, $\Delta H_{\Phi h-\Phi h}$), (■, $\Delta H_{\Phi h-K}$).

Figure 7. The dependence of phase transition temperatures on composition for the binary mixture of **P2** with **3**. a) second heating scan (❑, T_{K-K}), (❑, $T_{K-\Phi h}$), (Δ, $T_{\Phi h-\Phi h}$), (○, $T_{\Phi h-I}$); b) first cooling scan (●, $T_{I-\Phi h}$), (▲, $T_{\Phi h-\Phi h}$), (■, $T_{\Phi h-K}$).

Figure 8. The dependence of phase transition temperatures on the amount of $LiCF_3SO_3$ of the 10/90 (mole/mole) mixture of **P3** with **3**. a) first heating scan (❑, $T_{K-\Phi h}$), (○, $T_{\Phi h-I}$); b) second heating scan (❑, T_{K-K}), (❑, $T_{K-\Phi h}$), (Δ, $T_{\Phi h-\Phi h}$), (○, $T_{\Phi h-I}$); c) first cooling scan (●, $T_{I-\Phi h}$), (▲, $T_{\Phi h-\Phi h}$), (■, $T_{\Phi h-K}$); c) The dependence of ΔH associated with the phase transitions on the amount of $LiCF_3SO_3$ of the 10/90 (mole/mole) mixture of **P3** with **3** from first cooling scan (●, $\Delta H_{I-\Phi h}$), (▲, $\Delta H_{\Phi h-\Phi h}$), (■, $\Delta H_{\Phi h-K}$).

Figure 9. The dependence of phase transition temperatures on composition for the

binary mixture of **2** with **5**. a) second heating scan ($\square$, T_{K-K}), ($\square$, $T_{K-\Phi h}$), ($\square$, T_{K-I}), ($\bigcirc$, $T_{\Phi h-I}$); b) first cooling scan ($\bullet$, $T_{I-\Phi h}$), ($\blacksquare$, $T_{\Phi h-K}$), ($\blacksquare$, T_{I-K}); c) The dependence of ΔH associated with the transition temperatures for the binary mixture of **2** with **5** from first cooling scan ($\bullet$, $\Delta H_{I-\Phi h}$), ($\blacksquare$, $\Delta H_{\Phi h-K}$), ($\blacksquare$, ΔH_{I-K}).

Figure 10.   The dependence of phase transition temperatures on composition for the binary mixture of **4** with **5**. a) second heating scan ($\square$, T_{K-K}), ($\square$, $T_{K-\Phi h}$), ($\square$, T_{K-I}), ($\bigcirc$, $T_{\Phi h-I}$); b) first cooling scan ($\bullet$, $T_{I-\Phi h}$), ($\blacksquare$, $T_{\Phi h-K}$), ($\blacksquare$, T_{I-K}); c) The dependence of ΔH associated with the transition temperatures for the binary mixture of **4** with **5** from first cooling scan ($\bullet$, $\Delta H_{I-\Phi h}$), ($\blacksquare$, $\Delta H_{\Phi h-K}$), ($\blacksquare$, ΔH_{I-K}).

Figure 11.   The dependence of phase transition temperatures on the amount of $NaCF_3SO_3$ for the 50/50 (mole/mole) mixture of **2** with **5**. a) second heating scan ($\square$, T_{K-K}), ($\square$, $T_{K-\Phi h}$), ($\square$, T_{K-I}), ($\bigcirc$, $T_{\Phi h-\Phi h}$), ($\bigcirc$, $T_{\Phi h-I}$); b) first cooling scan ($\bullet$, $T_{I-\Phi h}$), ($\bullet$, $T_{\Phi h-\Phi h}$), ($\blacksquare$, $T_{\Phi h-K}$), ($\blacksquare$, T_{I-K}).

Table 1. Characterization of Compounds 1-5 and P1-P4.

Compound	Column Diameter (Å)	Thermal Transitions (°C) and Corresponding Enthalpy Changes (kcal/mru) in parentheses	
		Heating	Cooling
1	48.4	k 46(1.8) k 58(4.9) k 71(0.39) Φ_h 85(0.73) i k 45(1.8) k 48(-1.1) k 56(2.1) k 72(1.2) Φ_h 84(0.70) i	i 76(0.76) Φ_h 25(4.2) k
2	49.2	k 66(8.3) Φ_h 73(0.49) i k 66(8.3) Φ_h 73(0.45) i	i 65(0.74) Φ_h 35(9.5) k
3	58.2	k 56 (18.9) Φ_h 63 (0.80) i k 56 (13.3) Φ_h 61 (0.92) i	i 54 (0.62) Φ_h 34 (14.7) k
4	57.4	k 50(16.4) Φ_h 59(0.74) i k 49(15.5) Φ_h 57(0.88) i	i 52(0.78) Φ_h 31(15.1) k
5	--	k 61 (4.8) k 92 (18.6) i k 55 (2.7) k 91 (15.0) i	i 18 (12.4) k
P1	52.8	Φ_h 127(0.30) i Φ_h 127(0.30) i	i 110(0.38) Φ_h
P2	53.0	g 36 Φ_h 116(0.38) i g 37 Φ_h 116(0.30) i	i 103(0.38) Φ_h 29 g
P3	64.4	k 48(3.32) Φ_h 113(0.43) i Φ_h 112(0.43) i	i 103(0.45) Φ_h
P4	61.6	k 47(3.75) Φ_h 103(0.50) i Φ_h 99(0.43) i	i 87(0.69) Φ_h

a combined enthalpies for overlapped peaks
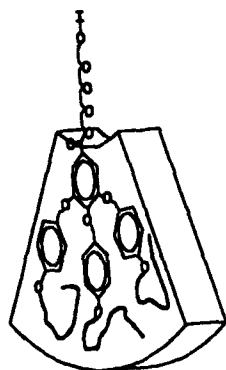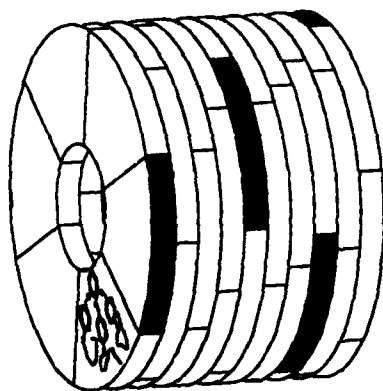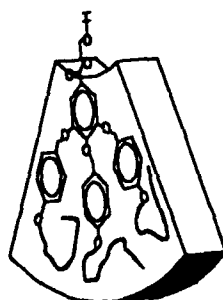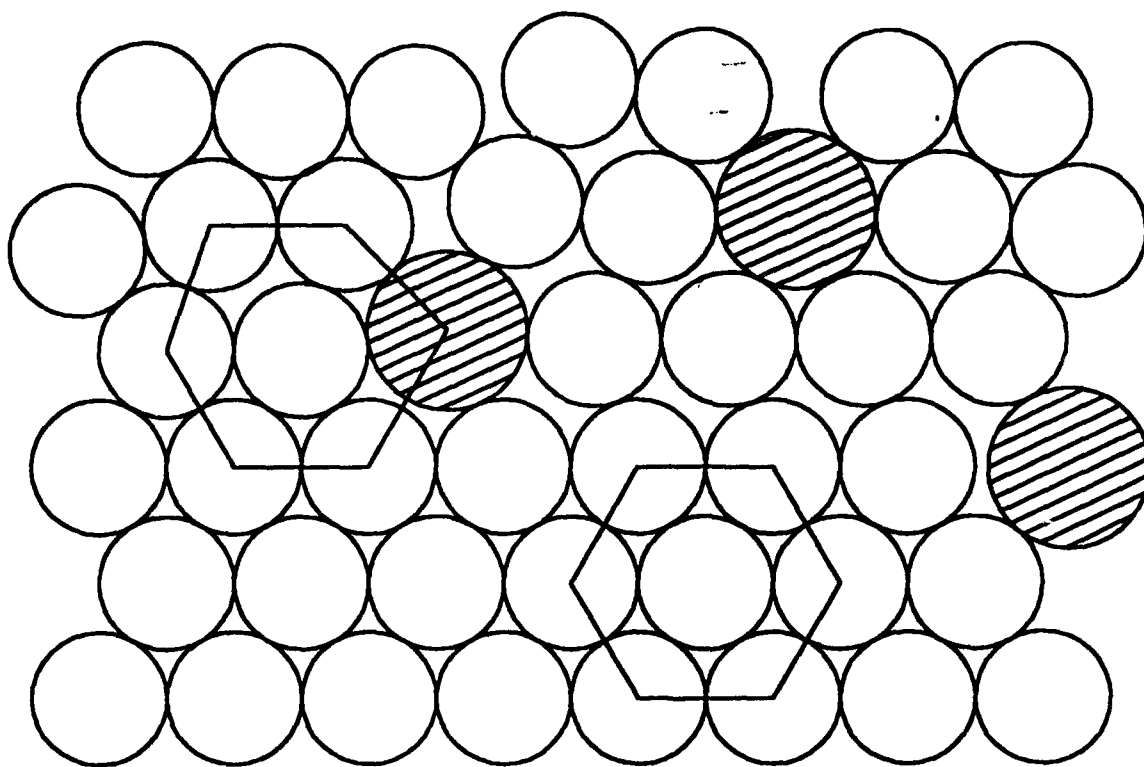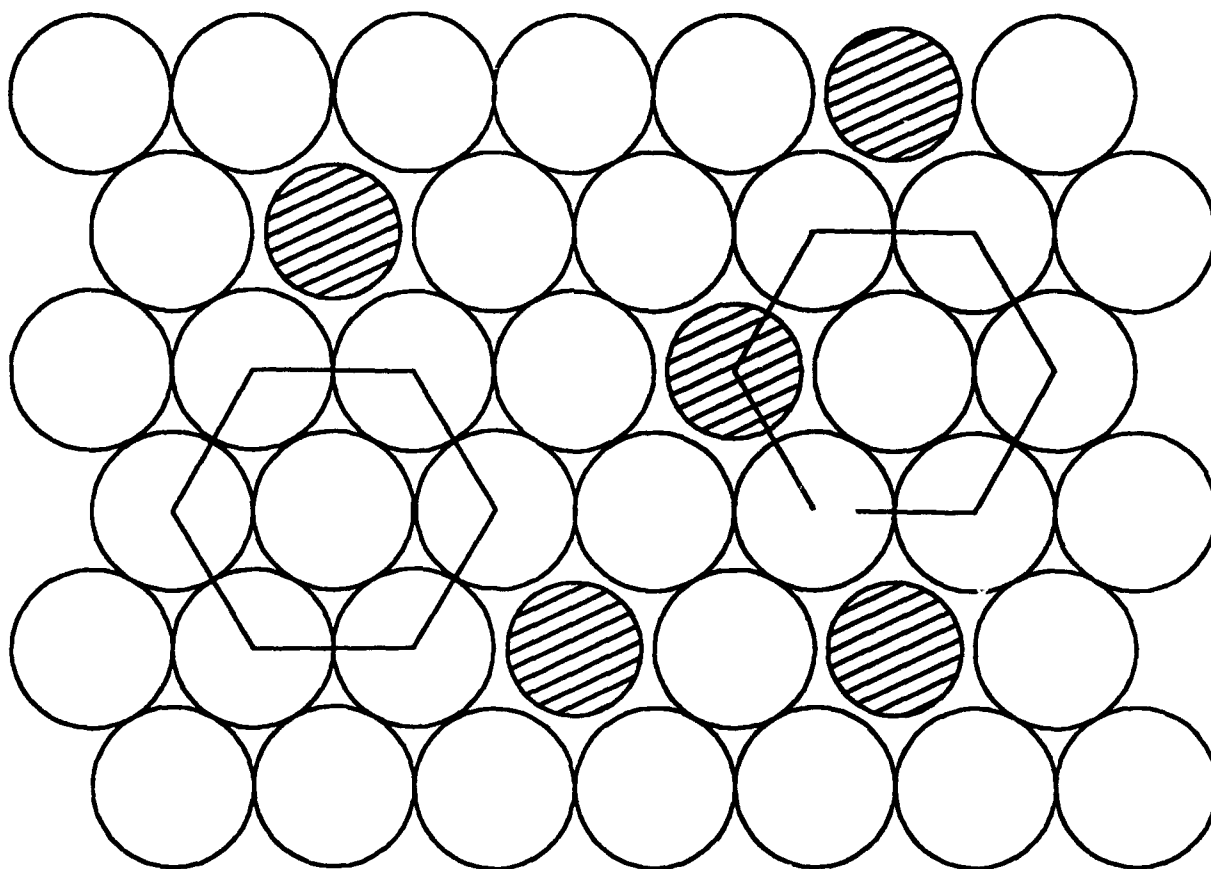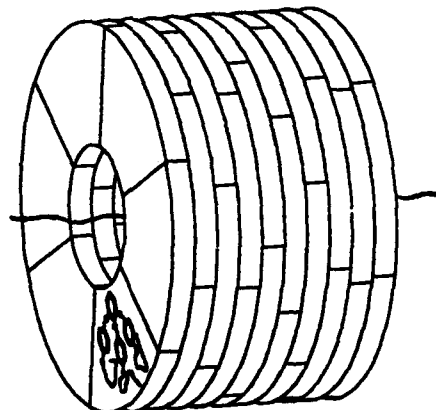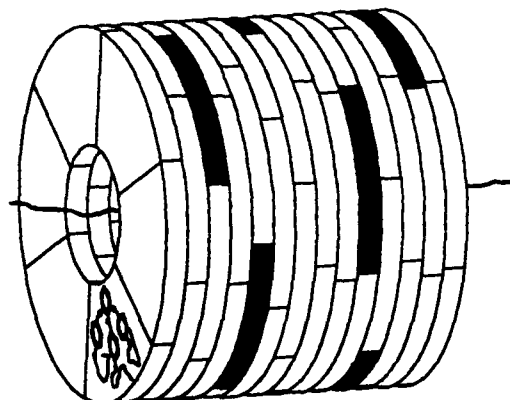
n=1 : **1**
n=2 : **2**
n=3 : **3**
n=4 : **4**

CH_3-$(CH_2)_{11}O$
CH_3-$(CH_2)_{11}O$
CH_3-$(CH_2)_{11}O$

CH_2O
CH_2O
CH_2O

n=1 : **P1**
n=2 : **P2**
n=3 : **P3**
n=4 : **P4**
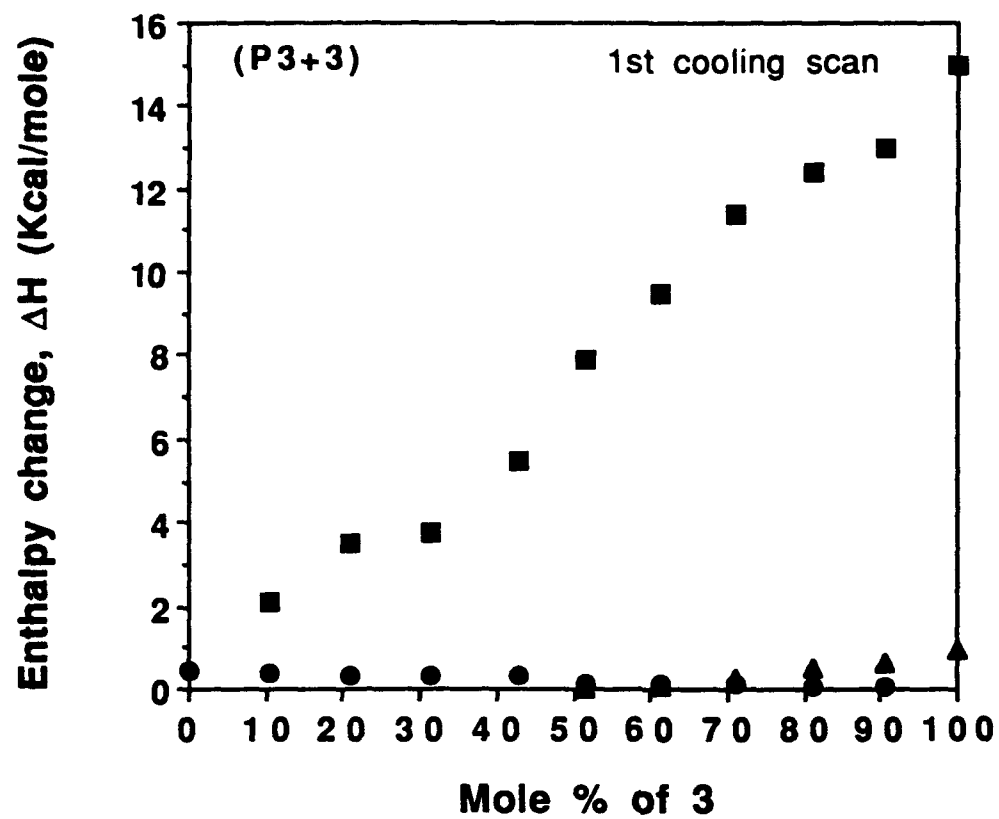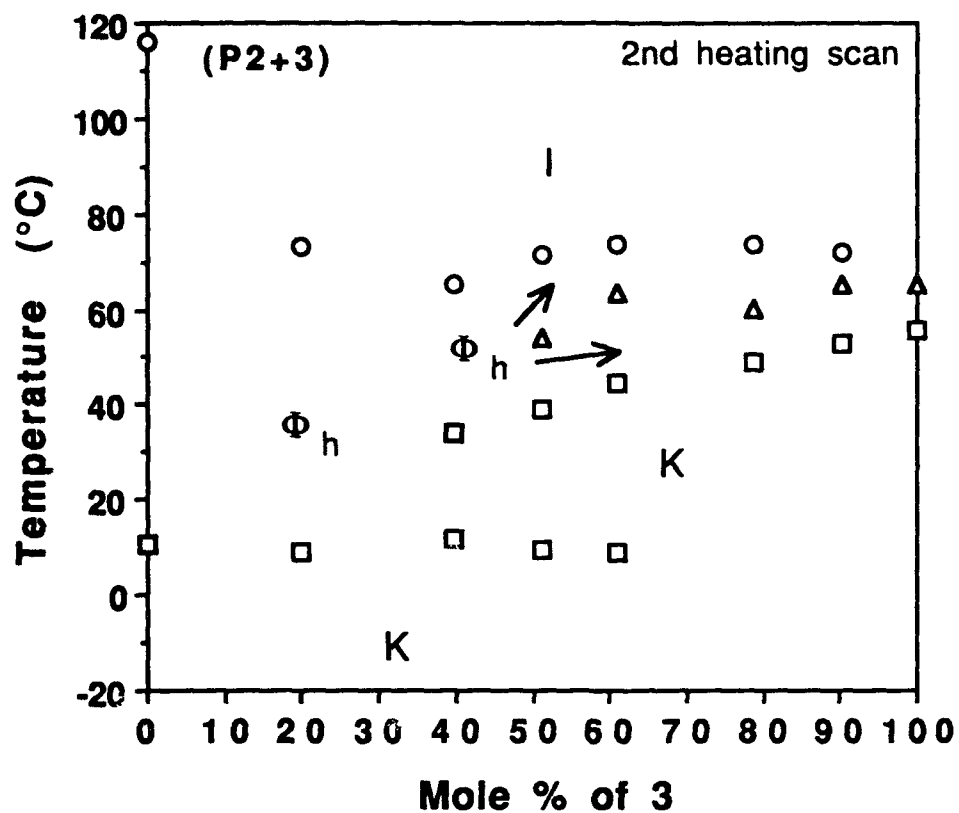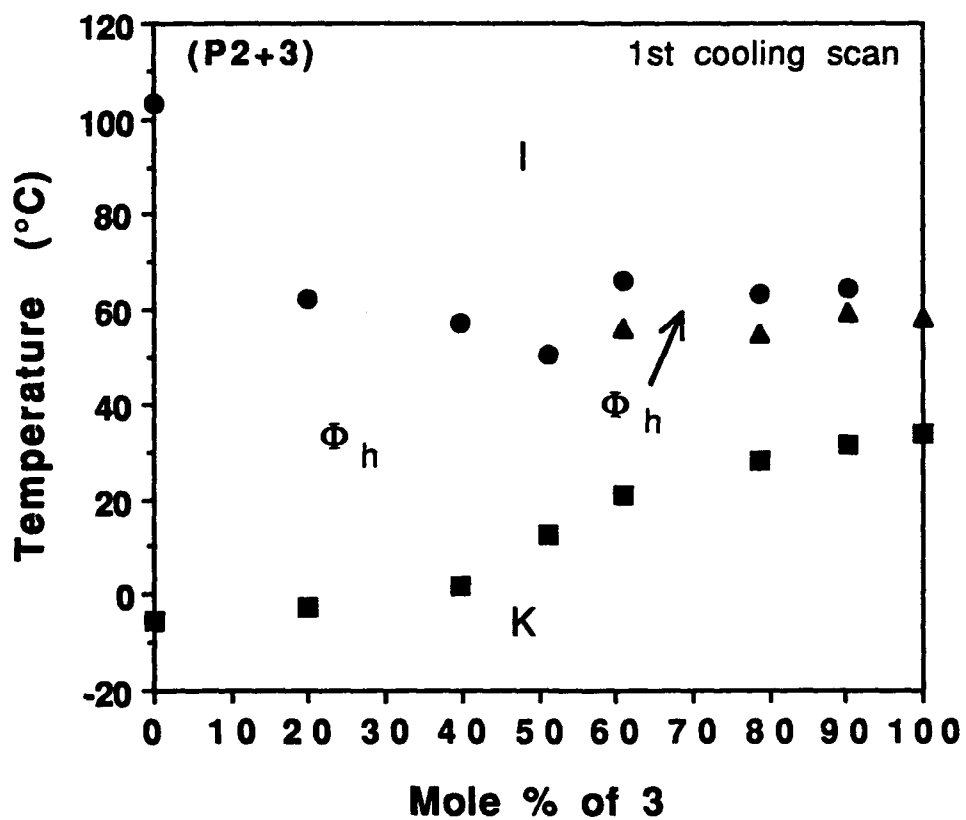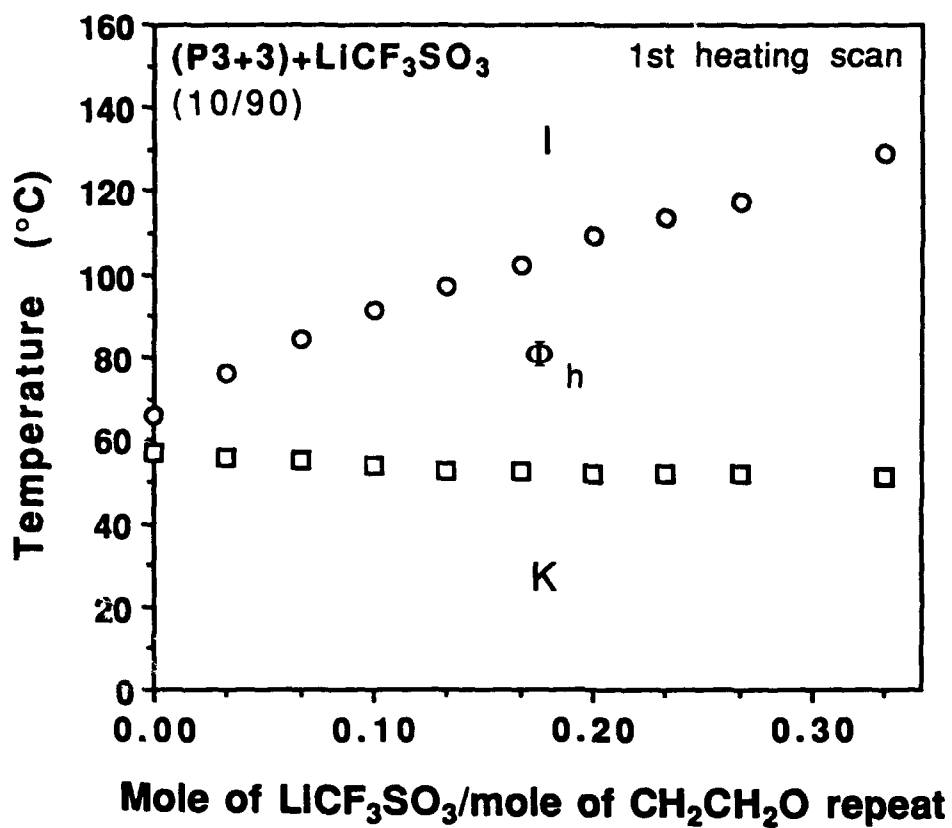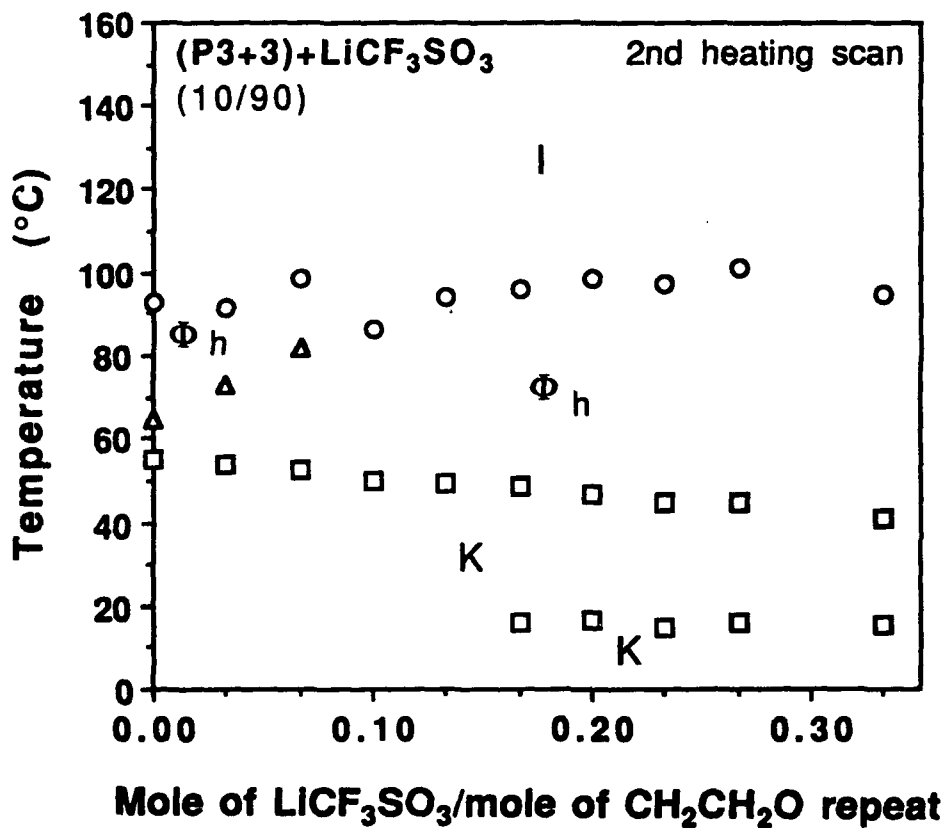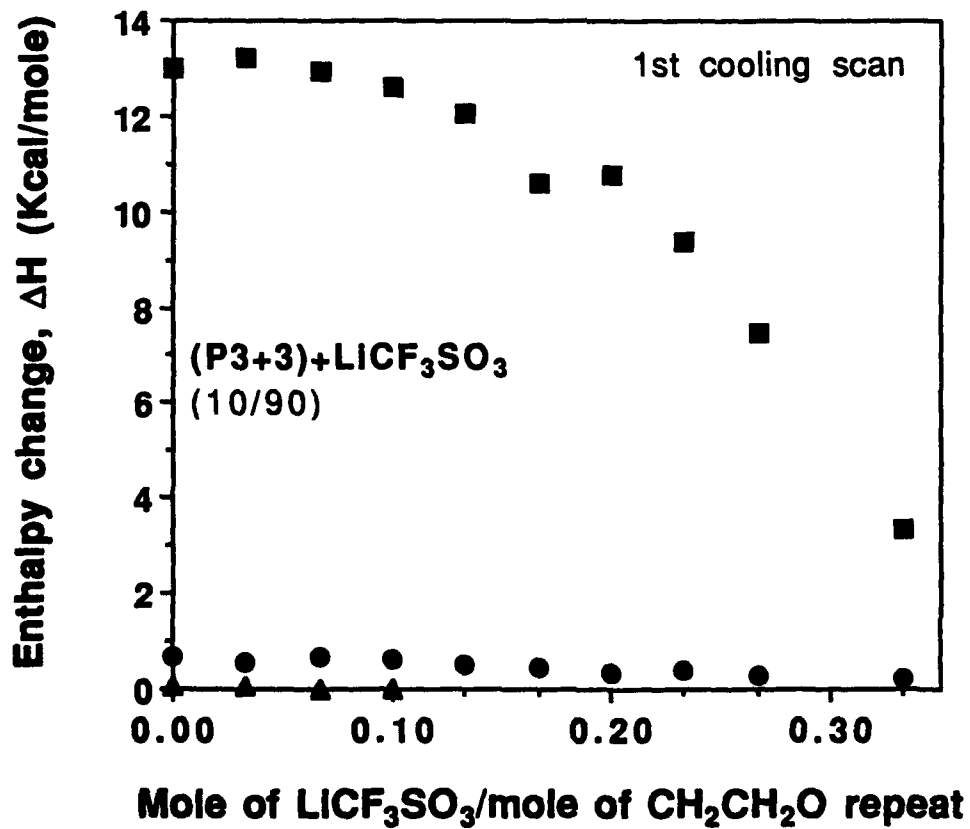
M^+

5

Scheme 1

Scheme 2

a)

b)

Scheme 3

3

P3

Scheme 4

a)

b)

Figure 1

a)

b)

Figure 2

a)

b)

Figure 3

a)

2nd heating scan   I   (P1+P4)

Φ_h

Φ_h

K

Temperature (°C)

Mole % of P1

b)

1st cooling scan   I   (P1+P4)

Φ_h

Φ_h

K

Temperature (°C)

Mole % of P1

Figure 4

c)

Figure 4

a)

2nd heating scan

I

Φ_h

(P3+P4)

K

Mole % of P3

Temperature (°C)

b)

1st cooling scan

(P3+P4)

I

Φ_h

K

Mole % of P3

Temperature (°C)

Figure 5

c)

Figure 5

a) (P3+3) 2nd heating scan

b) (P3+3) 1st cooling scan
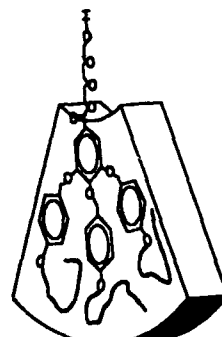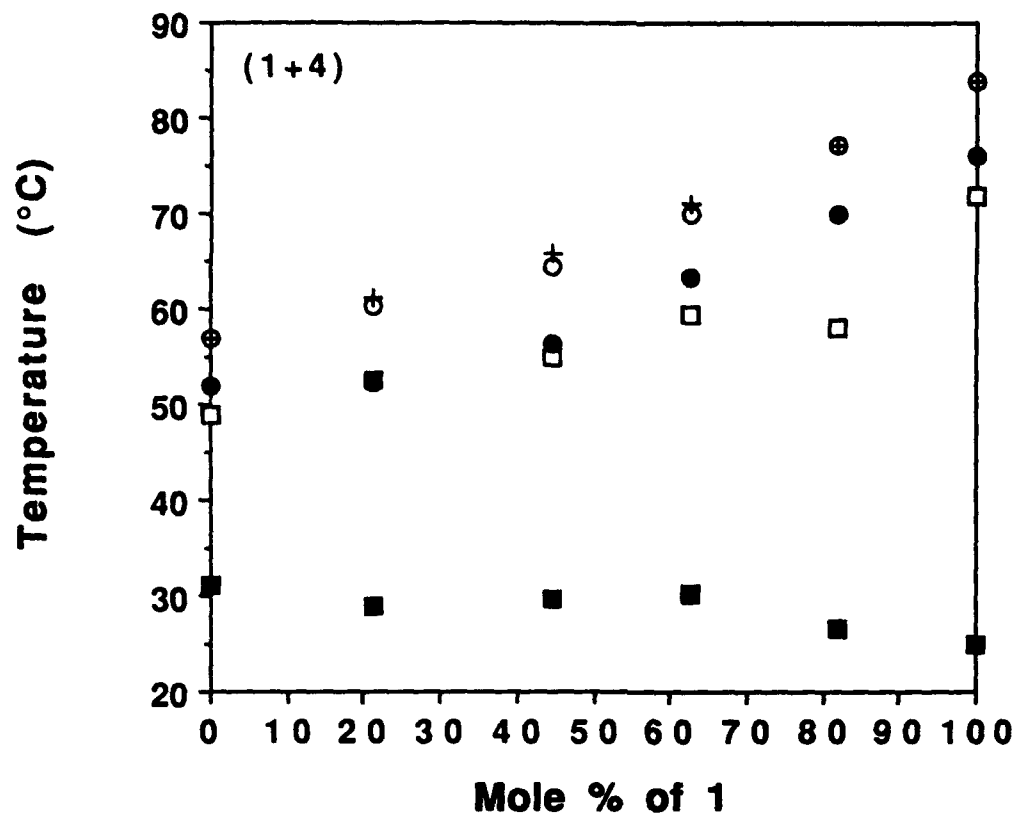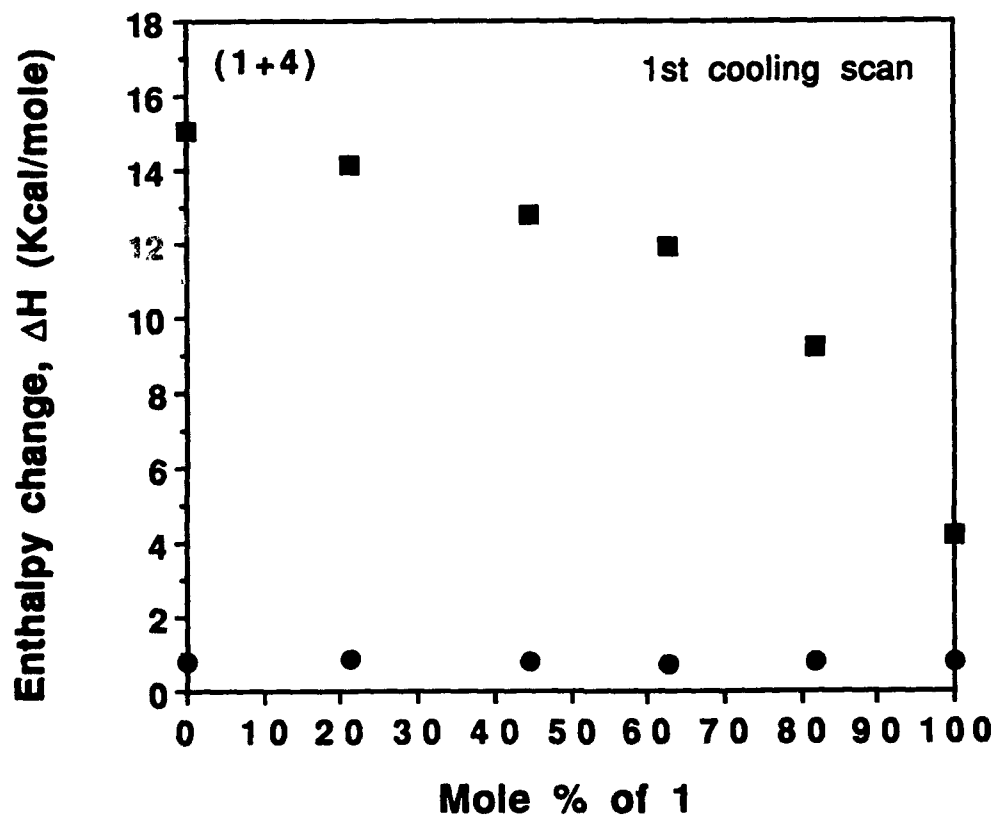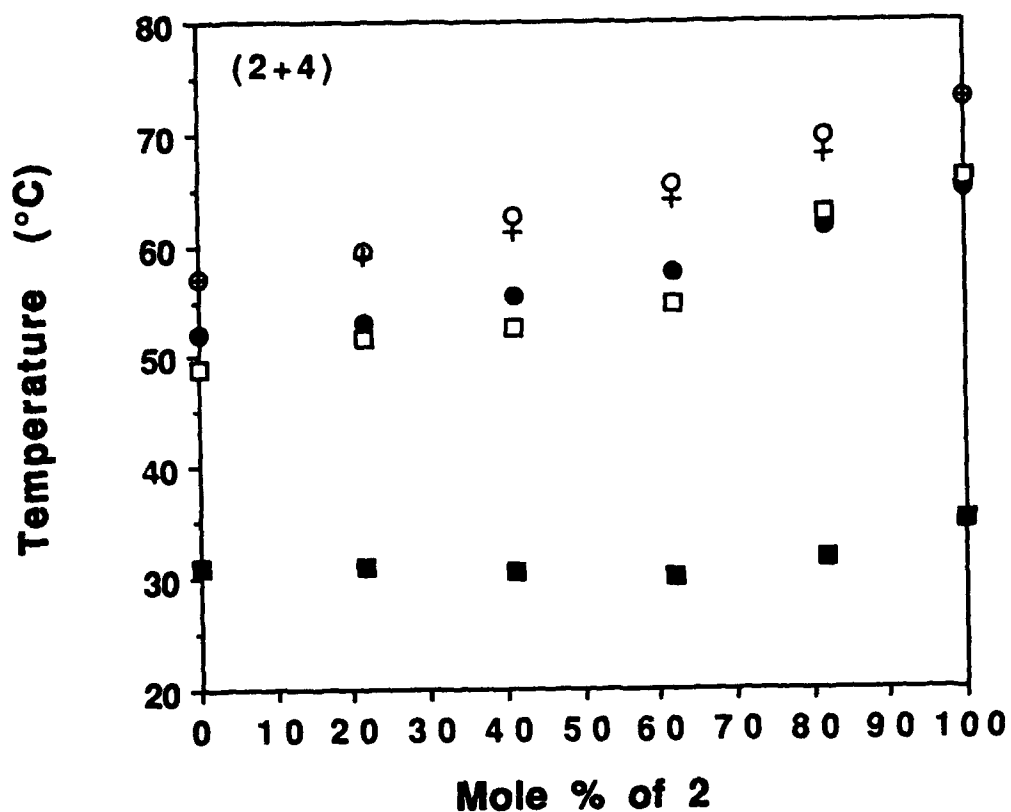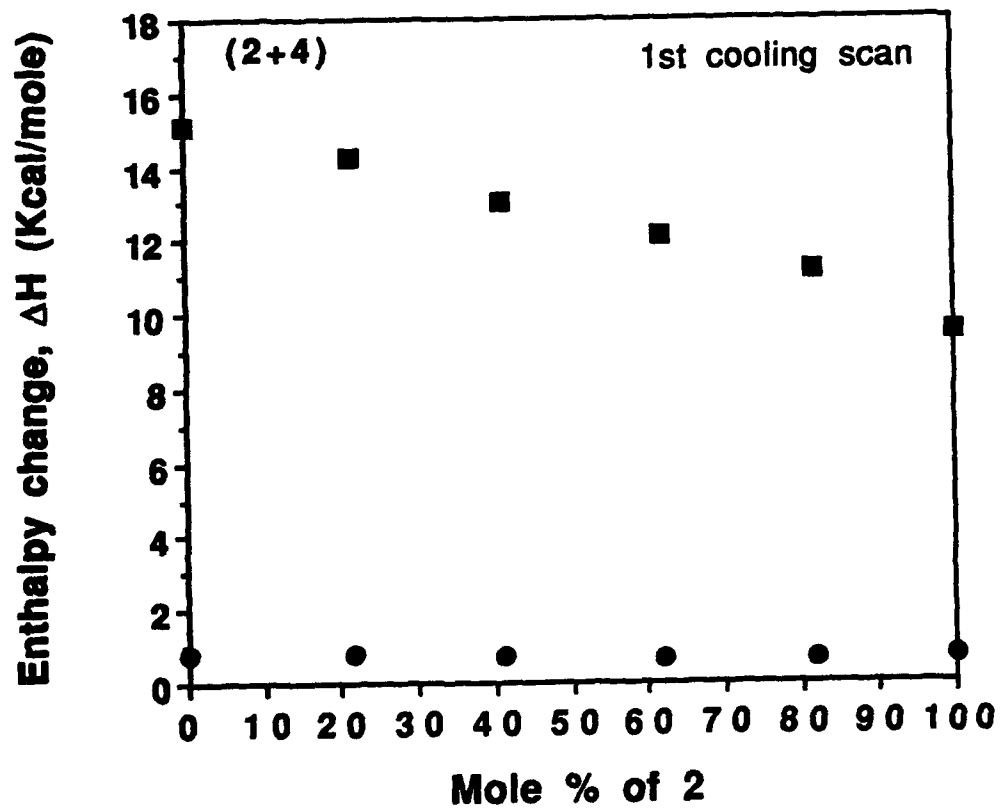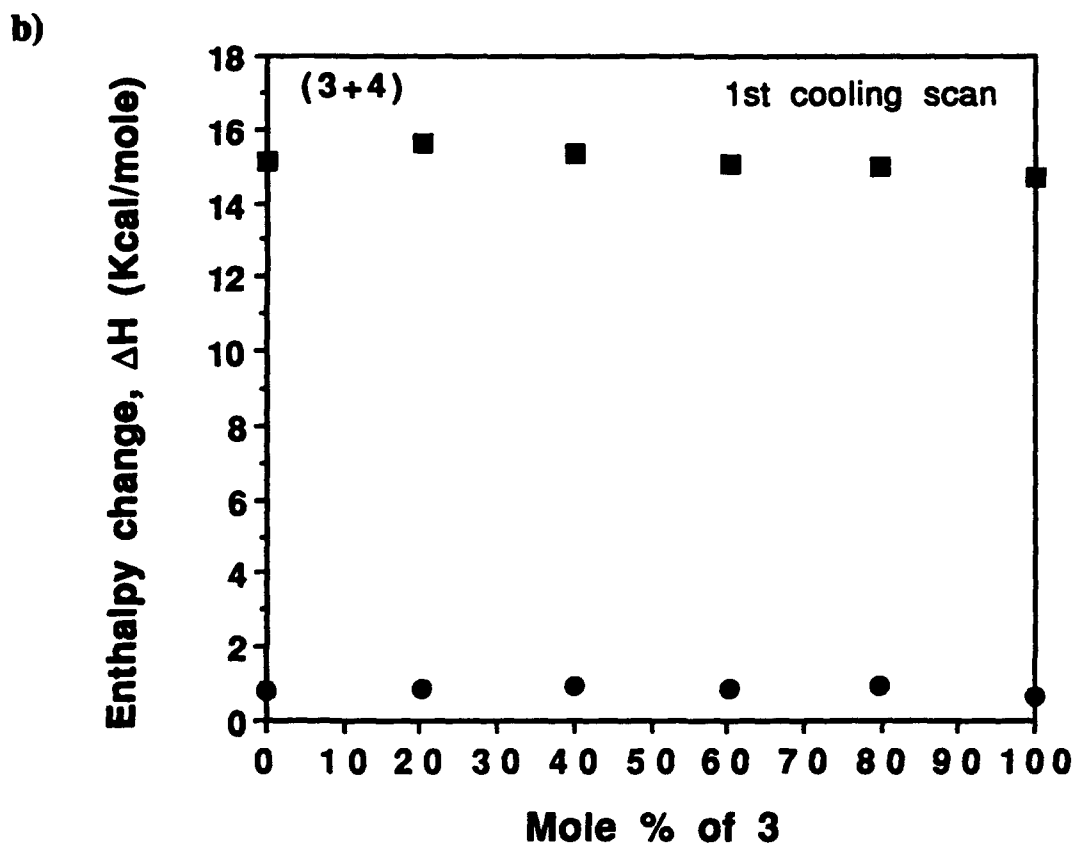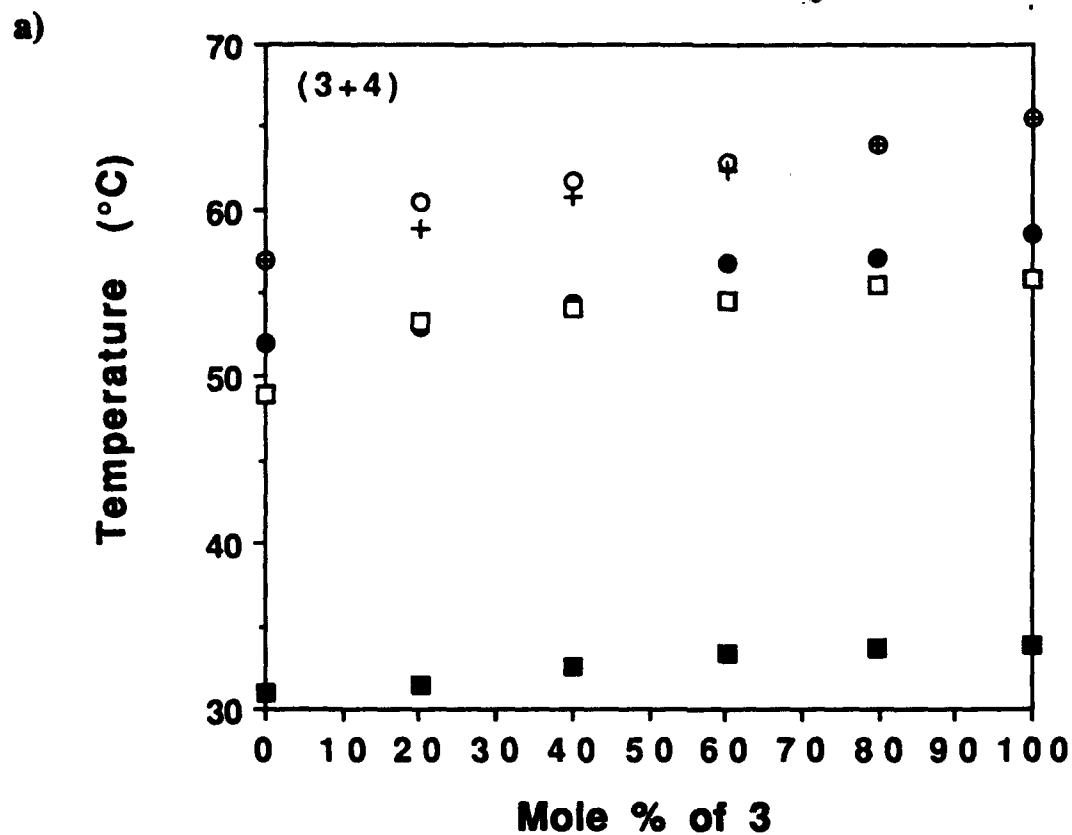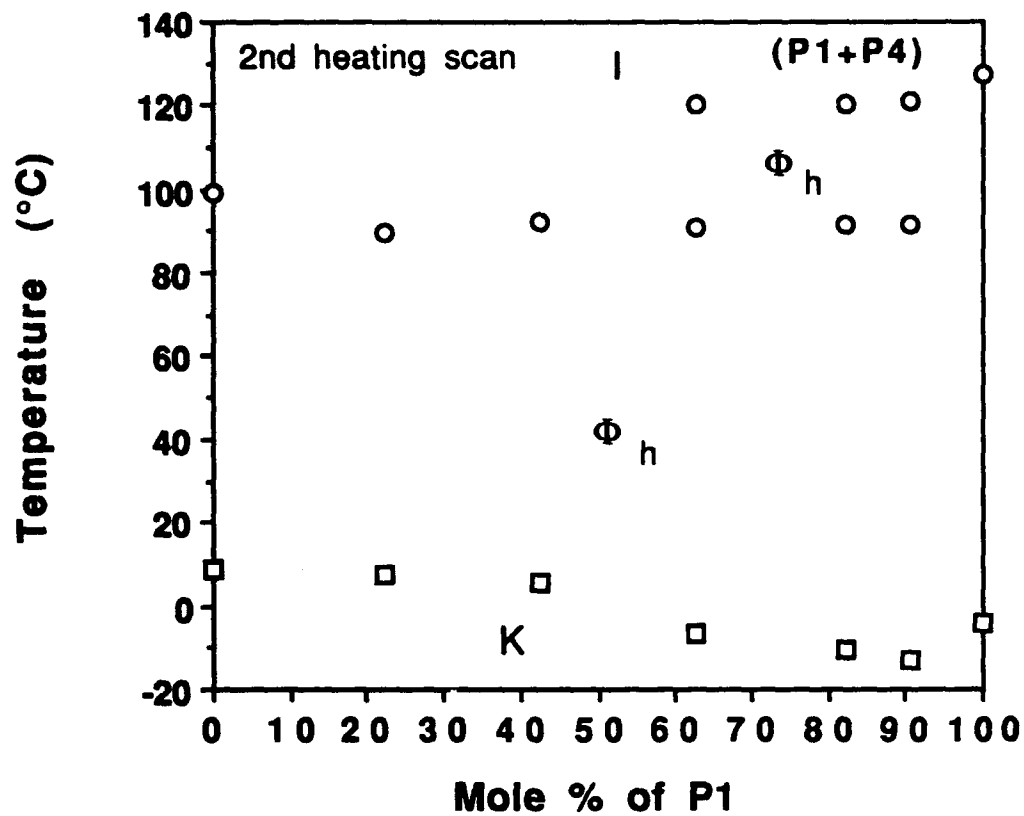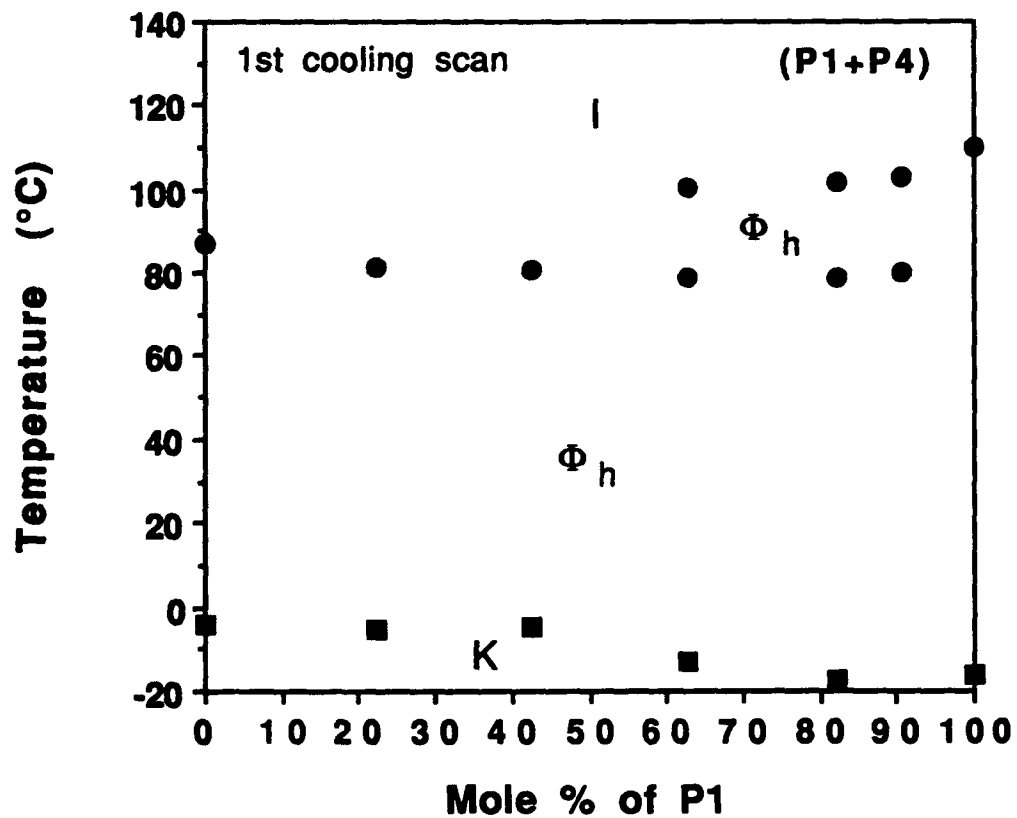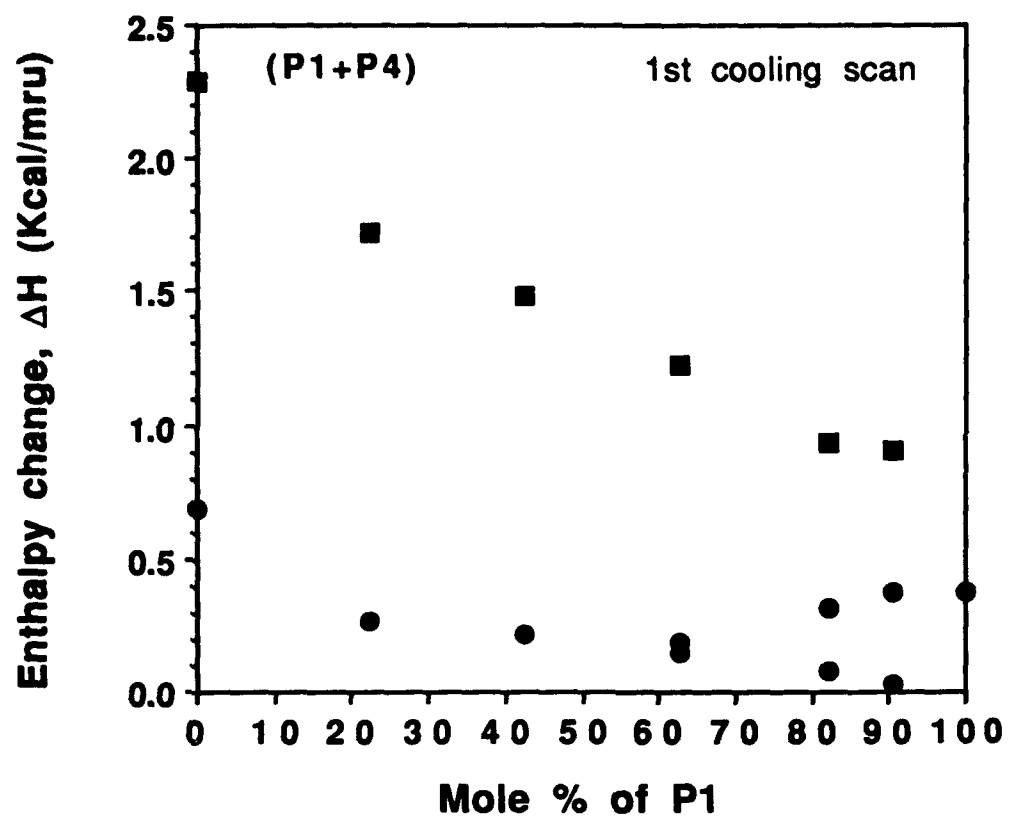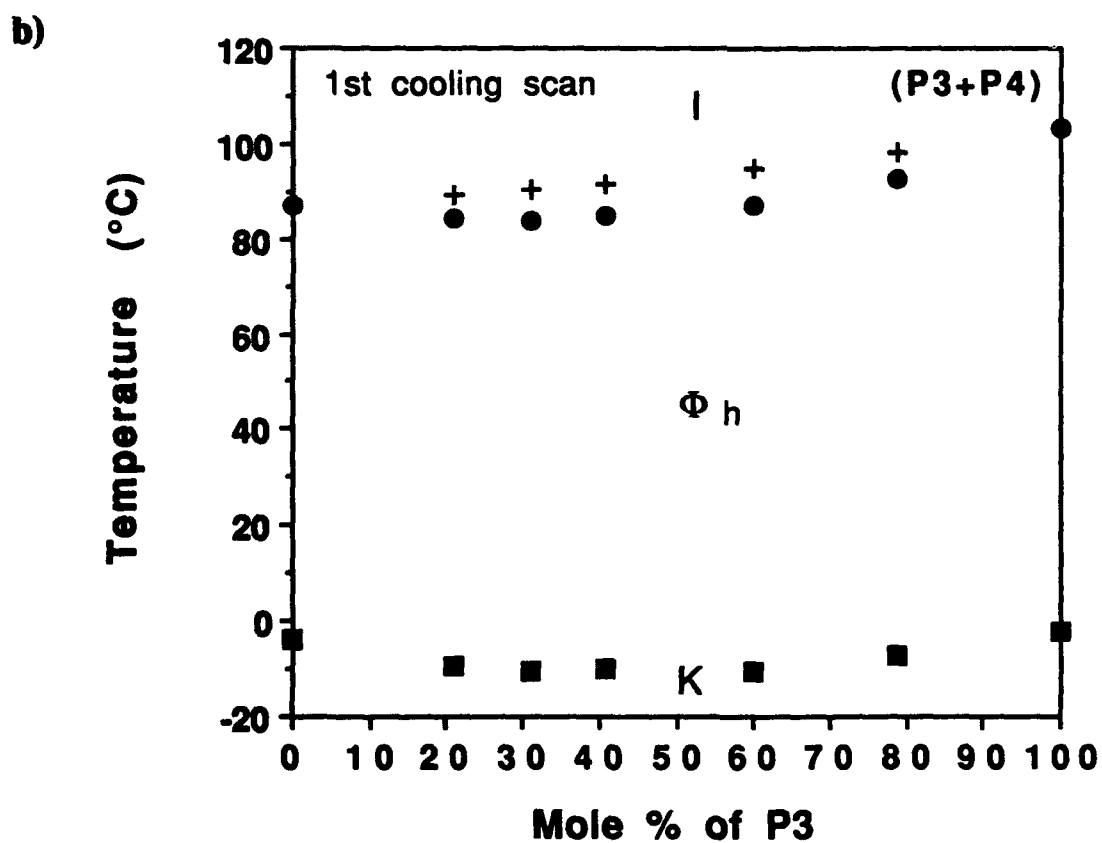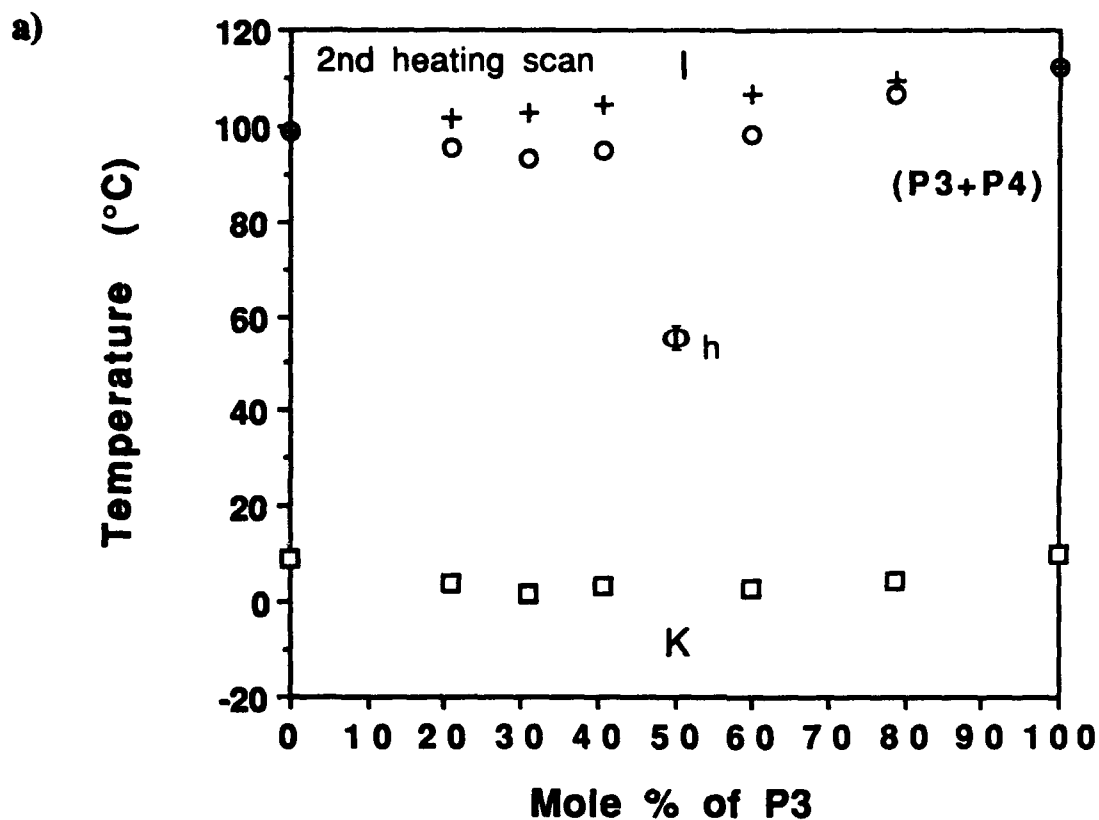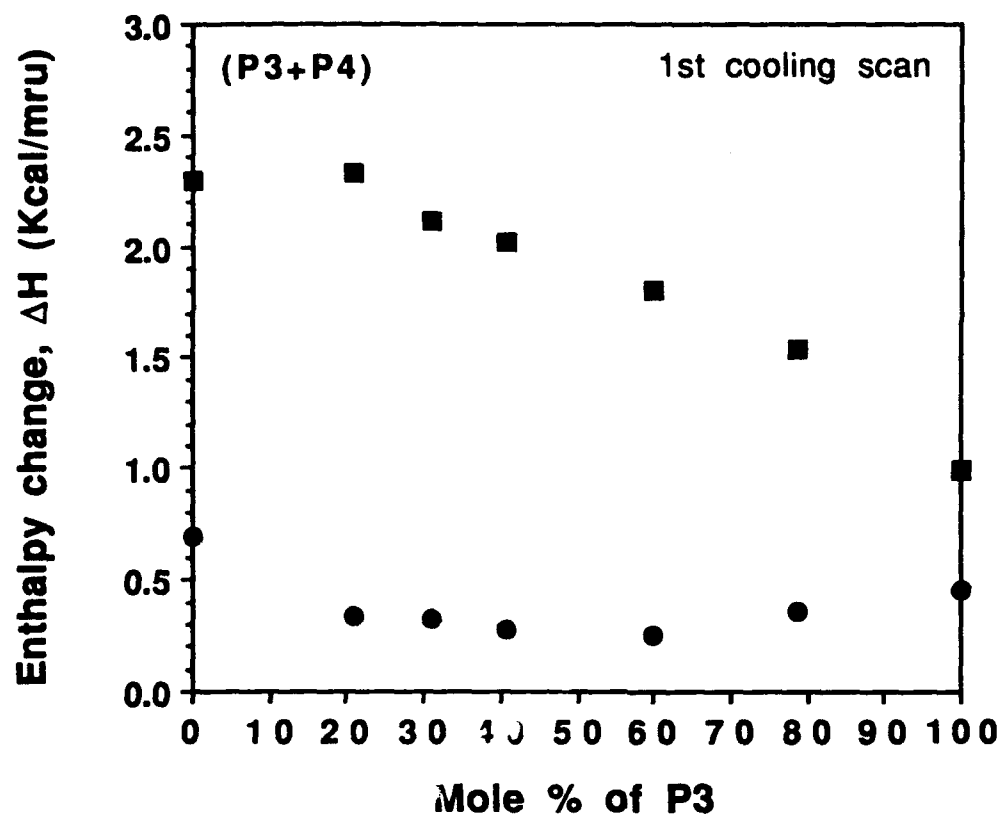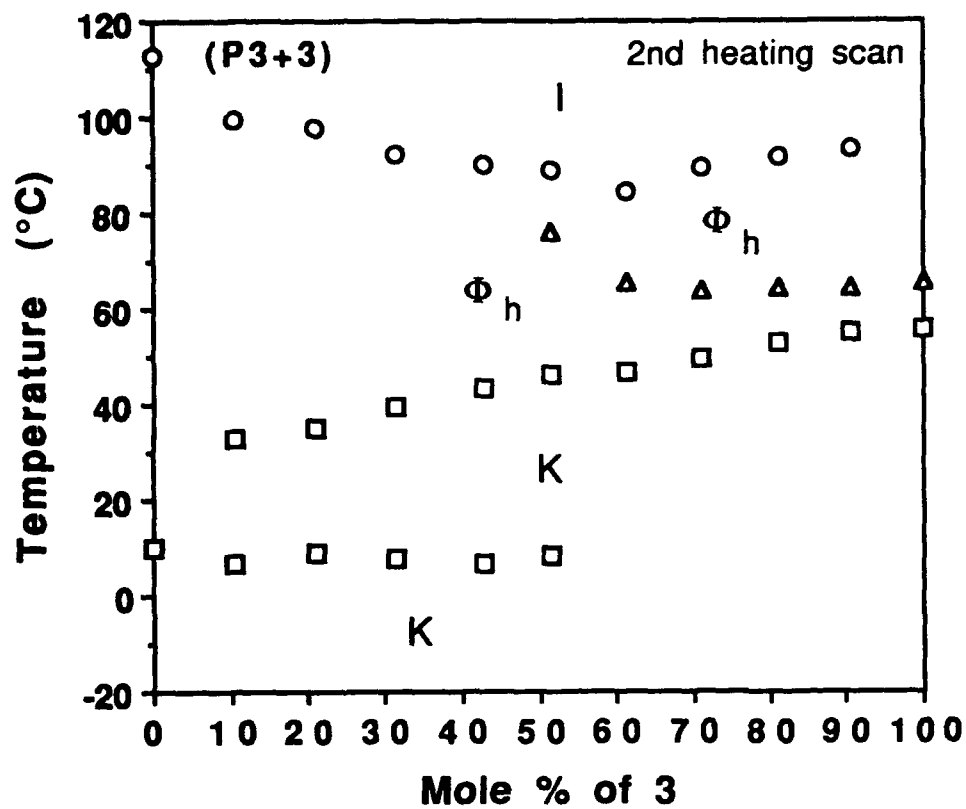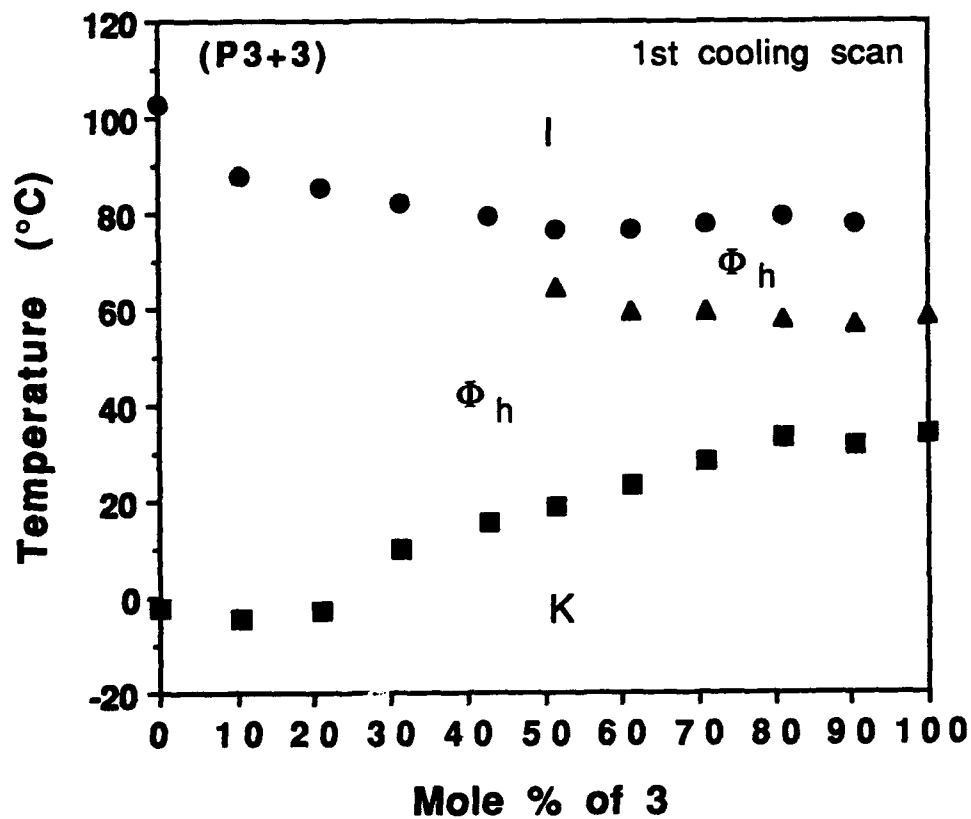
Figure 6

c)

Figure 6

a)

b)

Figure 7

a)

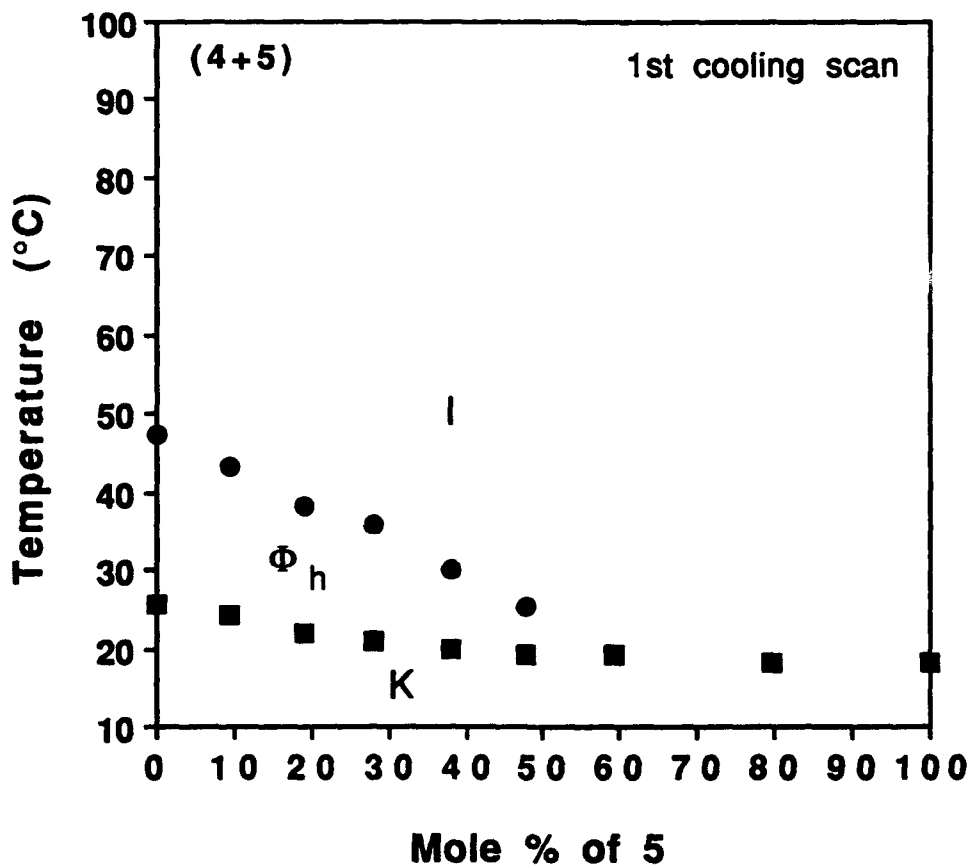Mole of LiCF₃SO₃/mole of CH₂CH₂O repeat

b)

Mole of LiCF₃SO₃/mole of CH₂CH₂O repeat
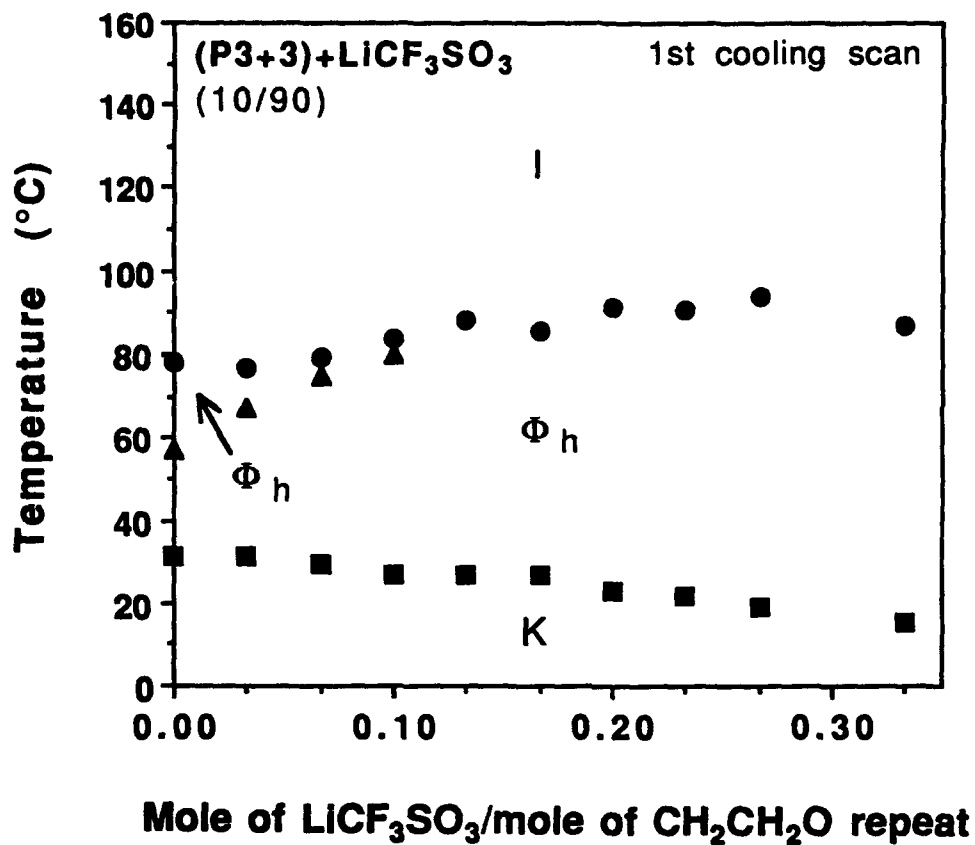
Figure 8

Figure 8

a)

b)

Figure 9

c)

Figure 9

Figure 10

c)

Figure 10

a)

(2+5) + NaCF₃SO₃ (50/50)   2nd heating

Temperature (°C) vs *Moles of NaCF₃SO₃/mole of 5*

b)

(2+5) + NaCF₃SO₃ (50/50)   1st cooling

Temperature (°C) vs *Moles of NaCF₃SO₃/mole of 5*

Figure 11